University of Alberta

Recommendations for Regulatory Implementation of Monitored Natural Attenuation at Contaminated Sites in Alberta

by

Anthony Paul Epp ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of **Master of Science**

in

Environmental Science

Department of Civil and Environmental Engineering

Edmonton, Alberta

Spring 2000

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ABSTRACT

Monitored natural attenuation (MNA) is rapidly gaining popularity in the United States as a remediation option for contaminated sites. Case studies indicate that natural attenuation processes are also potentially viable in Alberta's soil and climatic conditions.

In the United States, the Environmental Protection Agency (USEPA), Department of Defense (DOD), the American Society for Testing and Materials (ASTM), and several states have developed protocols and guidelines for use of MNA. In Europe, the United Kingdom is currently developing a protocol based on USEPA documents. The Netherlands has developed a decision-making guideline for evaluating MNA.

In Canada, no formal regulations regarding the use of natural attenuation currently exist. Two provinces, Ontario and Alberta, may consider MNA on a case-by-case basis. Alberta has begun development of a formal MNA policy. To assist this process, MNA documentation from other regulatory agencies was reviewed and options developed for an Alberta approach to MNA.

DEDICATION

For Dad and Mom,
Donna, Amanda and Megan

ACKNOWLEDGEMENT

First and foremost, I would like to thank my God who opened many doors for me in starting and completing this project. He has sustained me through the coursework and the times of doubt when the path seemed so difficult and the end seemed so far away.

Very special thanks go to my wife Donna and our children Amanda and Megan who endured four years of study, exams and thesis preparation. They are my greatest motivators and encouragers. I am also indebted to my parents, Henry and Irene, who's prayers and encouragement were so special.

I would like to thank my supervisor Dr. Warren Kindzierski for his faith in my abilities, his guidance and support in developing the research, and his support throughout the entire endeavour. I would also like to thank Dr. Kevin Biggar for his expertise, interest, and enthusiasm in the topic of natural attenuation and his invaluable assistance by sharing his own research for one of the case studies.

I would also like to express my thanks to the following people who aided in the gathering of data for the research and who were responsible for the final product.

- Ms. Dee Robinson, a fantastic wordsmith, who took my scribblings and made them legible.
- Ms. Lynn de Guzman, my unexpected research assistant, who found the most amazing articles and journals.
- Ms. Mica Wickramasekara, librarian with Alberta Environment, who was extremely helpful and patient with my numerous requests.

I would also like to thank my colleagues at Alberta Environment who have supported me throughout my scholastic career. Special thanks must be given to Dr. Robert Chandler, who gave me the opportunity to pursue my degree.

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List of Abbreviations

ADEC - Alaska Department of Environmental Conservation
AENV - Alberta Environment
ASTM - American Society for Testing and Materials
B.C. - British Columbia
BTEX - Benzene, Toluene, Ethylbenzene, Xylene
CAP - Corrective Action Plan
DCE - Dichloroethene
DIPA - Diisopropanolamine
DOD - United States Department of Defence
Eh^{o} - Redox Potential
FDEP - Florida Department of Environmental Protection
H_4MPT – Tetrahydromethanopterin
LUST - Leaking Underground Storage Tank
MDEQ - Michigan Department of Environmental Quality
MNA - Monitored Natural Attenuation
MOEE - Ontario Ministry of Environment and Energy
MOP - Monitoring Only Plan
MPCA - Minnesota Pollution Control Agency
MTBE - Methyl Tertiary Butyl Ether
NAD – Nicotinamide Adenine Dinucleotide
NHDES - New Hampshire Department of Environmental Services
NOB - Naturally Occurring Biodegradation
PCE - Perchloroethene
RCRA - Resource Conservation and Recovery Act
RNA - Remediation by Natural Attenuation
TEA - Terminal Electron Acceptor
TNT - Trinitrotoluene
TPOC - Temporary Point of Compliance
UDEQ - Utah Department of Environmental Quality

USEPA - United States Environmental Protection Agency
WDNR - Wisconsin Department of Natural Resources

1.0 INTRODUCTION

Natural attenuation of subsurface contaminants refers to the reliance on natural processes to act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in the soil and groundwater (USEPA, 1998). Natural attenuation includes a variety of physical, chemical, and biological processes including dispersion, advection, volatilization, adsorption and biodegradation.

Natural attenuation is also sometimes referred to as intrinsic bioremediation. However, it is evident from the definition of natural attenuation that intrinsic bioremediation forms only one component of natural attenuation. Intrinsic bioremediation relies on the innate capabilities of naturally occurring microbial populations to convert environmental pollutants to harmless forms (Lewandowski and DeFilippi, 1998). Madsen et al., (1991), Godsy et al., (1992), Davis et al., (1994), Lee et al., (1995), Wiedermeier et al., (1995), Cooley and Claffey (1996), Bradley and Chapelle (1997) and Landmeyer et al., (1998) report on sites where intrinsic bioremediation has been demonstrated to play a significant role in attenuating organic contaminants in groundwater.

Natural attenuation seems to be emerging as the remediation method of choice for contaminated sites in the United States. Wiedermeier et al., (1999) suggest that the primary motivation for considering natural attenuation as a potential remediation technology is the lack of efficient, cost-effective remediation technologies that can deal with the large number of contaminated sites across the nation. The authors point to problems associated with pump and treat systems and air sparging systems as support for this conclusion. It was indicated that pump and treat systems are initially effective in reducing contaminant concentrations but that after a while, concentrations in groundwater level off and the systems are no longer able to further reduce the concentration. Air sparging sets up a series of air channels through the subsurface from the injection point to the extraction point. The method is only effective in the vicinity of the channel (especially in low conductivity soils). Thus, an infinite number of channels would be required to remove the contaminant mass or to reduce concentrations to acceptable levels over the entire site.

There are several potential advantages to using natural attenuation at a site (USEPA, 1998 and 1999). There is less generation of remediation wastes thereby reducing the potential for cross-media transfer of contaminants. It is less intrusive to the site and there is no potential for facility downtime. It can be less disruptive to site development or redevelopment in that there are no extensive underground or aboveground mechanical structures or infrastructure to interfere with placement of other structures. It has the potential to be applied to all parts of the site and is not limited by surface structures. Natural attenuation reduces treatment impacts to habitats such as wetlands, which otherwise may be significantly affected by extensive and intrusive remediation methods. It can be used in conjunction with, or as follow-up to, other remediation methods. It also has potentially lower overall costs than active remediation methods. Natural attenuation may allow proponents to concentrate remediation dollars on sites with greater risks to receptors. Natural attenuation may be more protective of potential receptors. For example, with vapour extraction techniques for soil remediation, improper control of emissions may lead to unacceptable benzene exposures to onsite workers or offsite receptors. This would be avoided when natural attenuation is applied to the site.

Natural attenuation has several potential disadvantages associated with it (USEPA, 1998 and 1999). The cost of site characterization is generally much higher. Timeframes for completion of the remediation may be longer than conventional remediation methods. Natural attenuation may be affected by changes in site hydrogeology or geochemistry over time, particularly if site development or redevelopment occurs. Therefore, institutional controls may be necessary to ensure that natural attenuation processes are not affected and that receptors are protected while remediation is underway. Natural attenuation may not be clearly understood by the public requiring that proponents and regulators provide more extensive education and consultation efforts. Remediation by natural attenuation relies on empirical data generated from groundwater monitoring wells during site characterization and post-implementation monitoring. These wells are not always properly placed or may be rendered unusable due to changes in water levels or damage from equipment. The variability of groundwater data may also make effective evaluation of plume behavior difficult. In addition, biodegradation processes responsible for the removal of contaminants may result in intermediate compounds or degradation products that are more toxic than the original contaminant. Therefore, a proponent must be aware of potential degradation pathways and develop site characterization and monitoring programs accordingly. This adds costs to the overall remediation program.

Natural attenuation is not a passive or "do nothing" approach as has been suggested (Barker et al., 1989; Lewandowski and DeFilippi, 1998). In general, natural attenuation as it is applied at sites in the United States is accompanied by some measure of source control (USEPA, 1998). These control measures can include source removal (as in the case of contaminated soil or free phase product), containment of the source (as in the case of cutoff walls), or removal of an activity causing the source (as in the case of service station site decommissioning). Although no extraneous work is done to remove contaminants within the dissolved plume, considerable effort is involved in providing information to prove that the necessary natural attenuation processes exist. This extensive site and contaminant characterization is followed by comprehensive and long-term monitoring to evaluate the effectiveness of the natural attenuation processes in protecting potential receptors and preferably removing contaminants from the subsurface. Monitoring programs must also be able to detect changes in subsurface conditions (e.g. changes in hydrogeology or contaminant mass due to new sources) that can potentially alter effectiveness of the original natural attenuation processes. In the event that those changes cause significant effects, the monitoring program can be upgraded to accommodate those changes or a proponent can implement contingency plans developed for a site if additional, more intrusive remediation is required.

For natural attenuation to be accepted as a stand alone option for a site, attenuation processes and geochemical conditions at a site must not allow the rate of contaminant migration to exceed the rate of attenuation (i.e., a stable or shrinking plume). Therefore, a thorough understanding of site geology, hydrogeology, geochemistry, and microbiology is fundamental to the successful implementation of natural attenuation.

Natural attenuation has been demonstrated to be effective as a remediation option for a number of contaminants including fuel hydrocarbons, chlorinated solvents, and metals. Table 1-1 provides a compilation of chemicals that are amenable to natural attenuation processes based on literature review.

1.1 PROJECT DESCRIPTION

A review of the processes involved in natural attenuation was undertaken. Each process is described, and examples are given of contaminants that can be remediated by that process. Legislative requirements and guidance documents developed by regulators in Canada, the United States, and Europe were examined. These agencies accept the use of natural attenuation as a tool for managing contaminated sites. These documents are described to provide insight into different components of the legislation and to allow an understanding of pros and cons of the legislation and supporting protocols. Three case studies in Alberta were examined to determine whether application of natural attenuation is supported by site investigation data. Comparisons were made between the information provided by the case studies and information required by various legislation and technical protocols developed elsewhere. Finally, and most importantly, recommendations were made regarding necessary legislative and information requirements to support a policy on natural attenuation in Alberta.

Table 1-1. Compilation of Contaminants Amenable to Natural Attenuation Mechanisms

CONTAMINANT	NATURAL ATTENUATION PROCESSES
Methyl Tertiary Butyl Ether	Aerobic Biodegradation
Naphthalene	Aerobic Biodegradation, Sulphate Reduction, Methanogenesis
Benzene	Aerobic Biodegradation, Sulphate Reduction, Methanogenesis
Toluene	Aerobic, Anaerobic Biodegradation
Ethylbenzene	Aerobic, Anaerobic Biodegradation
Xylenes	Aerobic, Anaerobic Biodegradation
Chloroalkanes	Reductive Dechlorination
Chloroalkenes	Reductive Dechlorination, Aerobic Degradation
Carbon Tetrachloride	Cometabolism
Diisopropanolamine	Aerobic Biodegradation, Manganese Reduction, Iron (III) Reduction, Denitrification
Chloroform	Anaerobic Biodegradation
Metals	Adsorption, Cation Exchange, Hydrolysis
Methylene Chloride	Anaerobic Biodegradation
Bromoalkanes	Aerobic, Anaerobic Biodegradation
Radionucleides	Ion Exchange, Complexation
Sulfolane	Aerobic, Anaerobic Biodegradation
Trinitrotoluene	Denitrification, Sulphate Reduction
Polychlorobiphenyls	Aerobic Biodegradation
Vinyl Chloride	Anaerobic Biodegradation

1.2 OBJECTIVES

The objectives of this thesis are:

- Identify existing policy, legislation, and guidance on use of monitored natural attenuation as a remediation option for contaminated sites in North America and Europe
- Evaluate that legislation in terms of requirements to investigate, support, and implement monitored natural attenuation at a site and document those requirements for discussion
- Examine restrictions placed on use of monitored natural attenuation by regulators
- Present key points of existing legislation
- Examine case studies of contaminated sites in Alberta with regard to potential for natural attenuation and how information provided complies with existing regulatory legislation from environment agencies outside Alberta
- Provide guidance and recommendations for policy development on use of monitored natural attenuation as a remediation option in Alberta

2.0 NATURAL ATTENUATION PROCESSES

Important attenuation processes involved in and affecting the fate and transport of organic and inorganic contaminants dissolved in groundwater are discussed. Hydrodynamic dispersion, molecular diffusion, adsorption, dilution, volatilization, advection, and various chemical and biodegradation processes are discussed. The fate and transport of a contaminant is also controlled by its physical and chemical properties and the medium through which it travels.

Natural attenuation relies on the co-operative activities of several destructive and non-destructive processes. Only those processes that result in reduction of a contaminant's concentration are termed non-destructive. Examples of non-destructive processes are dispersion, dilution, and adsorption. Processes that result in the destruction of a contaminant's mass are termed destructive. Examples of destructive processes are biodegradation, chemical processes like oxidation, and biochemical processes like iron (III) reduction and methanogenesis.

Natural attenuation processes have been demonstrated for a wide variety of compounds and chemicals. Table 2-1 provides a summary of biotic and abiotic degradation processes for various organic compounds.

Table 2-1. Biological and Abiotic Degradation Mechanisms for Various Anthropogenic Organic Compounds (after USEPA, 1998).

Compound	Degradation Mechanism
Perchloroethene	Reductive Dechlorination
Trichloroethene	Reductive Dechlorination, Cometabolism
Dichloroethene	Reductive Dechlorination, Direct Biological Oxidation
Vinyl Chloride	Reductive Dechlorination, Direct Biological Oxidation
Trichloroethane	Reductive Dechlorination, Hydrolysis, Dehydrohalogenation
1,2-Dichloroethane	Reductive Dechlorination, Direct Biological Oxidation
Chloroethane	Hydrolysis
Carbon Tetrachloride	Reductive Dechlorination, Cometabolism
Chloroform	Reductive Dechlorination, Cometabolism
Methylene Chloride	Direct Biological Oxidation
Chlorobenzenes	Reductive Dechlorination, Direct Biological Oxidation, Cometabolism
Benzene	Direct Biological Oxidation
Toluene	Direct Biological Oxidation
Ethylbenzene	Direct Biological Oxidation
Xylenes	Direct Biological Oxidation
1,2-Dibromoethane	Reductive Dehalogenation, Hydrolysis, Direct Biological Oxidation

2.1 PHYSICAL PROCESSES

2.1.1 TYPES OF PROCESSES

2.1.1.1 Hydrodynamic Dispersion

Hydrodynamic dispersion is the process that spreads the contaminant plume parallel and at right angles to direction of groundwater flow and plume migration. It is generally the primary cause for dilution of a contaminant plume. Hydrodynamic dispersion can also result in migration of a plume into areas with additional electron acceptors, thereby enhancing the biodegradation of organic compounds.

Hydrodynamic dispersion is the sum of two components; mechanical dispersion and molecular diffusion. At low groundwater velocities, molecular diffusion may dominate. The effect of hydrodynamic dispersion on contaminant movement is illustrated in Figures 2-1 and 2-2. In Figure 2-1, hydrodynamic dispersion spreads the contaminant slug over a greater area and reduces its peak concentration at monitoring points downgradient of a source. In Figure 2-2, hydrodynamic dispersion reduces the contaminant concentration at the front of a plume and creates a zone of lower concentration moving in front of a contaminant plume.

2.1.1.1.1 Mechanical Dispersion

Mechanical dispersion is the dominant transport mechanism at normal groundwater velocities. The three processes responsible for mechanical dispersion and their effect on contaminant movement are illustrated in Figure 2-3.

The first process is the variation in flow velocity caused by groundwater movement through pore spaces of various sizes. As groundwater moves through a porous medium, it flows more slowly through larger pores than through smaller pores. The second process depends upon the flow path length or tortuosity. As groundwater moves through a porous medium, some of the water moves along less tortuous or shorter paths and some

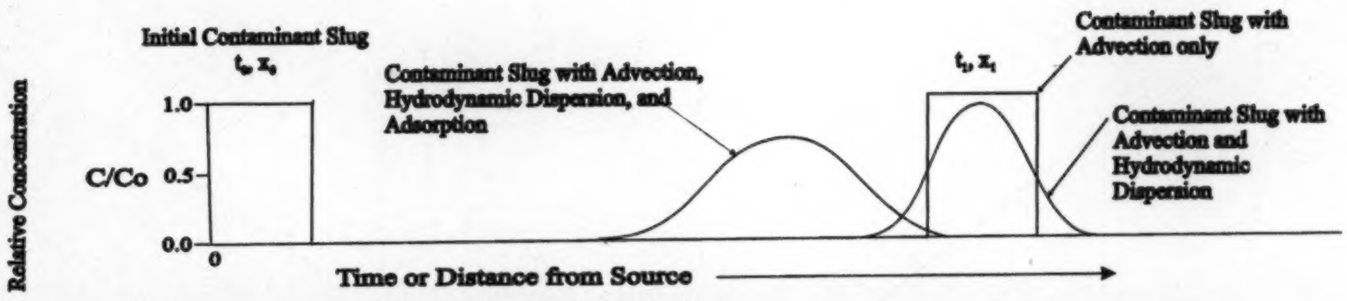


Figure 2-1. Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; and the combined processes of advection, hydrodynamic dispersion, and adsorption (after Wiedermeier et al., 1995).

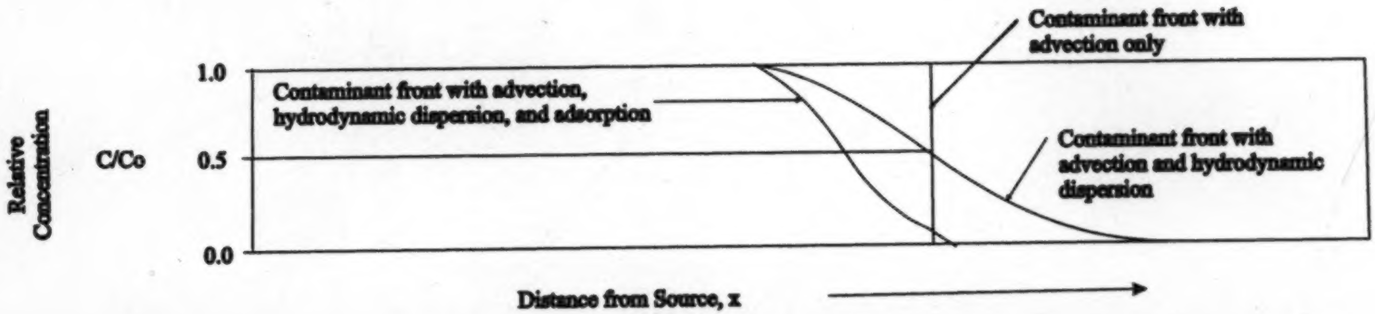
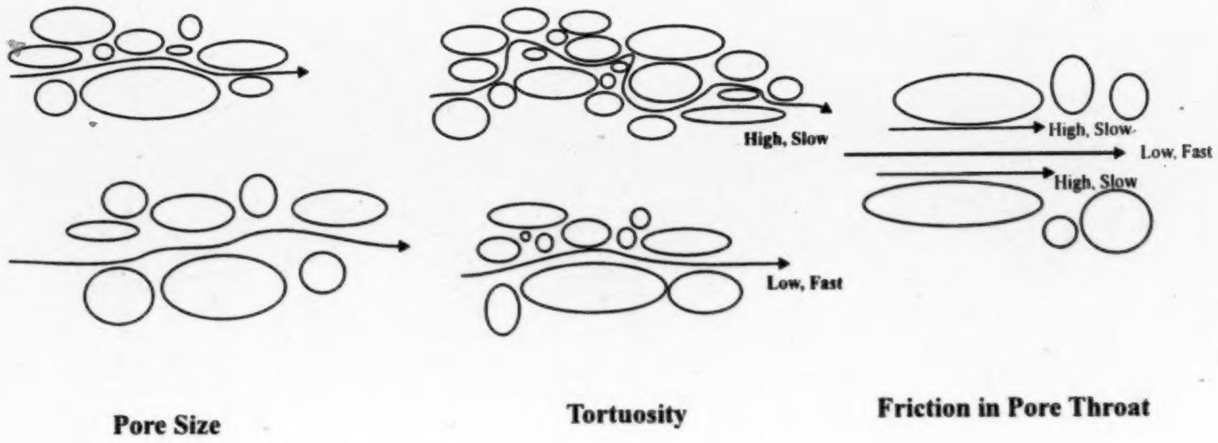


Figure 2-2. Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; and the combined processes of advection, hydrodynamic dispersion and adsorption (after Wiedermeier et al., 1995).

Figure 2-3. Physical Properties of Soil Causing Mechanical Dispersion at the Microscopic Scale.


High, Slow
Low, Fast
High, Slow
Low, Fast
High, Slow

Pore Size

Tortuosity

Friction in Pore Throat

along more tortuous or longer paths. The longer the flow path, the slower the average linear velocity of the groundwater and the dissolved contaminants. The third process is the variation in friction within an individual pore space. As with a pipe, groundwater flowing closer to the center of the pore has less friction acting on it than groundwater flowing next to the outer edges of the pore (i.e., in contact with soil grains adjacent to the pore space). Therefore, some of the dissolved contaminants will move faster than the average linear groundwater velocity and some slower. The overall result of dispersion is the mixing and spreading of contaminants within uncontaminated groundwater.

Dispersion may be divided into longitudinal and transverse components. Longitudinal dispersion occurs parallel to groundwater flow. Transverse dispersion occurs at angles to the direction of groundwater flow due to the effect of tortuosity. Tortuosity and pore size cause the flow paths through the aquifer materials to branch out from the plume centerline (Fetter, 1988). As a result, the front of a dissolved plume travels faster than would be predicted solely by calculating the average groundwater flow rate.

2.1.1.1.2 Molecular Diffusion

Molecular diffusion results when concentration gradients cause a solute to move from zones of higher concentration to zones of lower concentration. This occurs even in the absence of groundwater flow. Molecular diffusion is most important in groundwater systems with low velocities.

Fick's Laws describe the molecular diffusion of a solute (Wiedermeier et al., 1995). Under steady state conditions, Fick's First Law applies:

$$F = -D(dC/dx) \tag{1}$$

Where: F = mass flux of solute per unit of time (M/T),

D = diffusion coefficient (L^2/T),

C = solute concentration (M/L), and

dC/dx = concentration gradient ($M/L/L^3$).

Fracture systems within bedrock allow for diffusion of contaminants into the rock matrix as long as concentration gradients towards the matrix continue (Parker et al., 1994). Once matrix diffusion is complete, clean water flushing through a fracture sets up a reverse concentration gradient from the matrix to the clean water resulting in recontamination of that part of the groundwater. The time it takes for diffusion from matrix to water is often longer than diffusion from water to matrix due to much lower concentration gradients.

2.1.1.3 Dilution

Dilution of the chemical contaminant, whether by the chemical entering the groundwater system or by water infiltrating down into the groundwater system, has two basic effects. The first effect is that the chemical concentration in an aquifer system is reduced. The second effect is that re-aeration of the aquifer can occur and with it introduction of new electron acceptors. The introduction of oxygen via recharge can be enough to shift the dominant biodegradation process (Vroblesky and Chapelle, 1994).

2.1.1.4 Volatilization

Although volatilization does remove contaminants from the aquifer, it is not a destructive attenuation mechanism. Henry's Law governs partitioning of a contaminant between the liquid phase and the gaseous phase. The Henry's Law constant for a chemical determines its tendency to partition between the dissolved phase in groundwater and the gaseous phase in the soil gas. Henry's Law states that the concentration of a compound in the gaseous phase is directly proportional to the compound's concentration in the liquid phase. This relationship is a constant for the chemical.

The Henry's Law constant can be calculated by (Stumm and Morgan, 1996):

$$H/RT = C_a/C_w \tag{2}$$

Where: H = Henry's Law constant (atm*m^3/mol),
C_a = concentration of chemical in air (mol/m^3),
C_w = concentration of chemical in water (mol/m^3),
R = gas constant (atm*m^3/mol*K), and
T = temperature (K).

2.1.1.5 Advection

Advection is the transport of a dissolved contaminant by the bulk movement of groundwater. Advection is the most important process driving contaminant migration in groundwater (Wiedermeier et al., 1995). In the direction parallel to groundwater flow, the linear groundwater velocity caused by advection is given by (Freeze and Cherry, 1979):

$$v_x = [(K/n_e)(dH/dL)] \tag{3}$$

Where: v_x = average linear velocity in the x direction (L/T),
K = hydraulic conductivity of the subsurface medium (L/T),
n_e = the effective porosity of the medium (L^3/L^3),
H = hydraulic head (L), and
dH/dL = the hydraulic gradient (L/L).

When transport of dissolved contaminants occurs by advection alone, the plume has a sharp concentration front. Ahead of the front of a plume, the concentration is the same as background (barring the presence of some other contaminant source). Behind the plume front, the concentration is the same as the initial concentration at the point of release.

This is observed by an examination of the contaminant slug and contaminant front due to advection only shown in Figures 2-1 and 2-2. Contaminant movement in this fashion is referred to as plug flow. In actuality, the plume spreads out due to the processes of dispersion and diffusion discussed above.

2.2 CHEMICAL PROCESSES

2.2.1 ADSORPTION

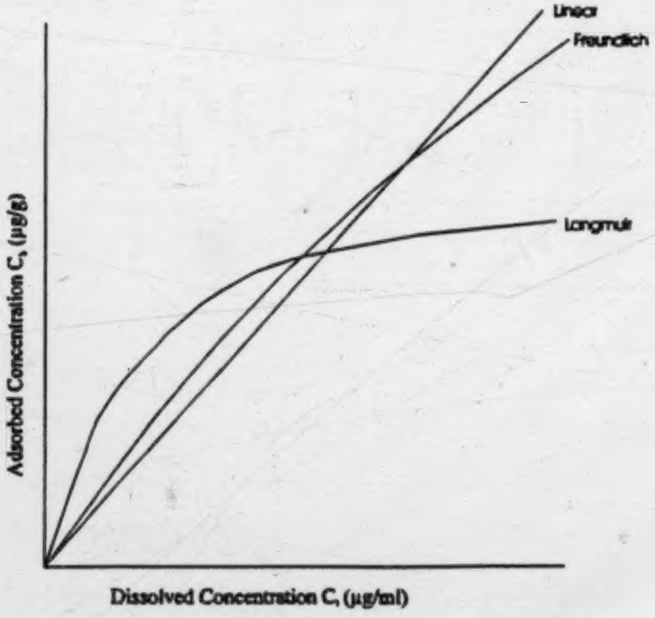
The chemical processes that contribute to natural attenuation include adsorption and chemical (abiotic) reactions (ASTM, 1998). Adsorption is controlled by chemical forces and interactions within and between a contaminant plume and aquifer materials. It has an effect on a contaminant's mobility, as well as rates of other transport and transformation reactions. Adsorption can be considered a chemical process because it does not result in an irreversible change in the contaminant.

Adsorption refers to the process involving partitioning of dissolved contaminants from groundwater and then adhering to particles making up aquifer materials through which a contaminant plume travels. Therefore, adsorption results in slowing the movement of a contaminant relative to groundwater flow velocity, a reduction in solute concentration, and potentially an increase in soil phase concentration of a contaminant. Because of these phenomena, adsorption can also influence rates of volatilization and biodegradation.

Adsorption of dissolved contaminants is a complex phenomenon caused by several mechanisms including London-van der Waals forces, Coulomb forces, hydrogen bonding, ligand exchange, chemisorption (covalent bonding between chemical and aquifer matrix), dipole-dipole forces, dipole induced dipole forces, and hydrophobic forces (Wiedermeier et al., 1995). Hydrocarbons most commonly exhibit adsorption through hydrophobic forces due to their nonpolar molecular structure. When the surfaces of aquifer matrix material are less polar than a water molecule, there is a tendency for hydrocarbons to adsorb to the matrix material. Clay minerals and organic matter in aquifer matrix have the greatest effect on adsorption. Colloidal organic material also adsorbs nonpolar organic chemicals (Stumm and Morgan, 1996).

The amount of a contaminant that will adsorb to the aquifer matrix material can be studied by bench-scale experiments (batch tests) where various concentrations of the contaminant are placed in solution with differing amounts of organic matter or clays. Once equilibrium has been reached, the amount of contaminant left in solution is measured. The relationship between the concentration of contaminant adsorbed and the concentration remaining in solution is called the adsorption isotherm (Wiedermeier et al., 1995). Three types of isotherm models are observed: the Langmuir isotherm, the Freundlich isotherm and the Linear isotherm, which is a variation of the Freundlich isotherm. Figure 2-4 illustrates the relationship between the different isotherms.

Figure 2-4. Characteristic Adsorption Isotherm Shapes (after Wiedermeier et al., 1995)



The Langmuir isotherm describes a non-linear relationship between the contaminant concentration adsorbed and the concentration remaining in solution. At high concentrations the relationship becomes almost a constant. The Freundlich isotherm is generally more applicable to dilute solutions and results in a near linear relationship. The empirically derived Freundlich isotherm is defined by the following equation (Stumm and Morgan, 1996):

$$C_s = mC_w^n \tag{4}$$

Where: C_s = quantity of adsorbate associated with the adsorbent (mol/Kg),
m = Freundlich constant,
C_w = total chemical concentration of adsorbate in solution (mol/litre), and
n = measure of nonlinearity involved (unitless).

Where the linear isotherm applies, it is generally valid for a dissolved species that is present at a concentration less than one-half of its solubility. The distribution coefficient, K_d, is used to describe the distribution of a chemical between the aquifer matrix material and the aqueous phase. It is the ratio of the adsorbed contaminant concentration and the dissolved contaminant concentration. It is also the slope of the isotherm describing the partitioning behavior of the dissolved contaminant. The higher the distribution coefficient, the greater the potential for the contaminant to be adsorbed to the aquifer matrix materials. For nonionic organic compounds, K_d, can also be determined from the following equation (Wiedermeier et al., 1995):

$$K_d = (K_{oc})(f_{oc}) \tag{5}$$

Where: K_{oc} = soil adsorption coefficient, and
f_{oc} = fraction of organic carbon in an aquifer matrix.

In areas with little organic matter content, clay minerals become the dominant adsorption sites in the aquifer matrix. The distribution coefficient can also be determined using laboratory batch tests as described above. Aquifer samples should be obtained from the most transmissive zone in the aquifer. These zones also tend to have the lowest organic content resulting in a conservative calculation of adsorption.

The coefficient of retardation, R, is used to estimate the retarded contaminant velocity. It is given by (Wiedermeier et al., 1995):

$$R = 1 + [(\rho_b K_d)/n] \tag{6}$$

Where: R = coefficient of retardation (dimensionless),
ρ_b = bulk density of the aquifer (M/L^3),
K_d = distribution coefficient (L^3/M), and
n = aquifer matrix porosity (L^3/L^3).

The retarded velocity of an adsorbed contaminant, v_c, is then given by:

$$v_c = v_x/R \tag{7}$$

Where: v_x = linear groundwater velocity, given by $v_x = Ki/n$
K = hydraulic conductivity of the aquifer material (m/s),
i = hydraulic gradient, and
n = porosity of the aquifer materials.

2.2.2 ABIOTIC PROCESSES

Abiotic chemical reactions refer to those reactions that do not involve metabolically active microorganisms or extracellular enzymes (ASTM, 1998). For metals, abiotic processes can include adsorption and precipitation. With organic contaminants, abiotic processes refer to destructive processes that are not facilitated by biological means. The results of an abiotic reaction may produce intermediate compounds that are more or less toxic than the parent contaminant, or compounds that are more or less easily biodegraded. Abiotic processes for organic compounds include:

a) Hydrolysis, which occurs when an organic chemical reacts with either water or a hydroxide ion to produce an alcohol;
b) Substitution, which occurs when an organic chemical reacts with another anion as the nucleophilic agent; and
c) Elimination, which is the loss of two adjacent groups within a molecule and results in the formation of a double bond.

During hydrolysis, if the alcohols are halogenated, additional hydrolysis of an organic compound to acids or diols may occur. The addition of a hydroxyl group to the original organic compound may either make it more susceptible to biodegradation or make the compound more soluble (USEPA, 1998). The number of halogen substituents partly controls the likelihood that a halogenated solvent will undergo hydrolysis. The more substituents present, the less likely that hydrolysis will occur. Other factors that can affect the likelihood of hydrolysis are the location of a halogen substituent on the carbon chain and the pH of the aquifer system. Vogel et al., (1987) indicate that the presence of clays, which can act as catalysts during hydrolysis, may also increase the rate of hydrolysis.

Chlorinated ethanes can undergo hydrolysis to end products of ethanol (Vogel et al., 1987) and acetate (Jeffers et al., 1989). However, as the number of chlorine atoms increases, dehydrohalogenation may become the more important abiotic process. Hydrolysis of 1,1,1-trichloroethane results in intermediate compounds of 1,1-dichloroethane, and chloroethane with an end product of ethanol.

Dehydrohalogenation is an elimination reaction involving halogenated alkanes in which a halogen is removed from one carbon atom, followed by subsequent removal of a hydrogen atom from an adjacent carbon atom (USEPA, 1998). This two-step reaction produces an alkene. The likelihood that dehydrohalogenation will occur increases with an increase in the number of halogen substituents. During dehydrohalogenation of chloroethane, Vogel et al., (1987) reported an end product of vinyl chloride.

2.2.3 METALS HYDROLYSIS

Metals hydrolysis refers to reactions of hydrated metals with protons and hydroxides in solution to form metal hydroxide precipitates. Polymeric hydrolysis species have been reported for most metal ions (Stumm and Morgan, 1996). The hydrolyzed species form a dimer (a multinuclear hydrolysis product) by a condensation process. The dimer may undergo additional hydrolytic reactions that could provide additional hydroxyl groups which, in turn, could form more bridges. A sequence of hydrolytic and condensation reactions under conditions of oversaturation with respect to the metal hydroxide leads ultimately to the formation of precipitates. A study by Swindoll et al., (1997) of natural remediation of metal constituents at a chemical manufacturing facility in Delaware indicated that precipitation and sorption were responsible for attenuation of dissolved metals in groundwater. The processes were directly affected by microbial activity. As microorganisms degraded available organic material, pH, redox potential, and availability of reactive species such as ligands in groundwater were altered. Groundwater at the site was also supersaturated with aluminum, barium, iron, and calcium. These metals would react with sulphate, carbonate, or phosphate in groundwater and form insoluble precipitates.

2.2.4 ION EXCHANGE

In general, ion exchange refers to any replacement of an ion in a solid phase in contact with a solution by another ion (Stumm and Morgan, 1996). In the context of natural attenuation, it refers to replacement of one adsorbed, readily exchangeable ion by another. The ion exchange capacity of a soil or soil minerals in solution (i.e., aquifer matrix materials) is the number of moles of adsorbed ion charge that can be desorbed from a unit mass of soil, under given conditions of temperature, pressure, soil solution composition, and soil solution mass ratio (Sposito, 1989).

Cationic radionuclides may be sorbed to the aquifer matrix materials by processes such as ion exchange or surface complex formation, thus retarding their transport by groundwater.

The exchange of ions between pore water and soil particles is not limited to aqueous ions such as copper, cadmium, or zinc. Ion pairs and complex species such as copper and zinc chloride or copper and zinc hydroxide exchange and adsorb with a variety of soil surfaces (Eccles, 1998). The most important adsorbing surfaces in these exchanges are the manganese and iron oxides.

2.3 BIOLOGICAL PROCESSES

Many organic and inorganic contaminants can be biodegraded by native populations of microorganisms in the subsurface. Since 1980, studies by Atlas (1981, 1984 and 1988), Barker et al., (1987, 1989), Godsy et al., (1992), Davis et al., (1994), Bradley and Chapelle (1995), Landmeyer et al., (1998) and others have shown that native populations of microorganisms can degrade hydrocarbons including components of gasoline, diesel, jet fuel and kerosene. Malone et al., (1993) showed that as the molecular weight of a hydrocarbon increases, so too does its resistance to biodegradation. Biodegradation of fuel hydrocarbons is mainly limited by availability of electron acceptors and will proceed until all of the contaminants biochemically accessible to the microorganisms are destroyed (USEPA, 1998). This holds true for dilute hydrocarbon concentrations. At high concentrations or in the presence of free-phase liquids, hydrocarbons may be toxic to microbiological populations in soil or groundwater.

Conversely, more highly chlorinated solvents are biodegraded under natural conditions via reductive dechlorination. This is a process that requires both electron acceptors and an adequate supply of electron donors. If electron donors are depleted in the subsurface before chlorinated solvents are reduced, the process of reductive dechlorination will stop.

Biodegradation is generally not accomplished by a single species of bacteria. Site contamination is usually a mixture of contaminants, and several bacteria species can utilize those contaminants and their biodegradation byproducts as substrate for growth. Prevalent bacteria are those that can out-compete others for substrates and nutrients. Table 2-2 lists bacteria grown on a mixture of benzene, toluene, xylene, naphthalene, styrene, and dicyclopentadiene (Hubert et al., 1999). This mixture represents contamination identified at a petrochemical facility in east-central Alberta (Site B in Case Study section). In this instance 16 different bacteria were grown on the substrate.

Table 2-2. Bacteria Population Grown in the Lab on a Hydrocarbon Mixture From a Petrochemical Facility in East-Central Alberta (Hubert et al., 1999).

Pseudomonas syringae	*Alcaligenes* sp.	*Sphingomonas yanoikuyae*	*Bacillus Benzeovorans*
Azospirillum sp.	*Agrobacterium rubi*	*Pseudomonas putida*	*Pseudomonas agarici*
Xanthomonas campestris	*Flavobacterium lutescens*	*Pseudomonas flavescens*	*Pseudomonas florescens*
Bacillus pseudomegaterium	*Bortadella parapertusis*	*Rhodococcus globerulus*	*Pseudomonas aureofaciens*

During biodegradation, microorganisms transform available nutrients to forms useful for energy and cell reproduction by accommodating the transfer of electrons from donor to acceptor. Figure 2-5 illustrates biodegradation of toluene via aerobic and anaerobic biodegradation processes. This figure clearly illustrates differences in amounts terminal electron acceptors utilized and the amounts of carbon dioxide and water produced by different biodegradation processes.

Figure 2-5. Biodegradation of Toluene Via Aerobic and Anaerobic Processes (after Wiedermeier et al., 1995).

AEROBIC PROCESSES

$$C_6H_5CH_3 + 9\ O_2 \Rightarrow 7\ CO_2 + 4\ H_2O \qquad (8)$$

ANAEROBIC PROCESSES

Denitrification

$$5\ C_6H_5CH_3 + 36\ NO_3^- + 36\ H^+ \Rightarrow 18\ N_2 + 35\ CO_2 + 38\ H_2O \qquad (9)$$

Manganese Reduction

$$C_6H_5CH_3 + 18\ MnO_2 + 36\ H^+ \Rightarrow 18\ Mn^{2+} + 7CO_2 + 22\ H_2O \qquad (10)$$

Iron (III) Reduction

$$C_6H_5CH_3 + 36\ Fe(OH)_3 + 72\ H^+ \Rightarrow 36\ Fe^{2+} + 7CO_2 + 94\ H_2O \qquad (11)$$

Sulphate Reduction

$$8\ C_6H_5CH_3 + 36\ SO_4^{2-} + 72\ H^+ \Rightarrow 36\ H_2S + 56\ CO_2 + 32\ H_2O \qquad (12)$$

Methanogenesis

$$8\ C_6H_5CH_3 + 40\ H_2O \Rightarrow 36\ CH_4 + 20\ CO_2 \qquad (13)$$

Electron donors, in the context of this thesis, include natural organic matter, chlorinated solvents, and fuel hydrocarbons. When these donors are not present in the subsurface in sufficient quantity to support the microorganisms that utilize them as the sole electron donors, the microorganisms can still degrade hydrocarbons but must utilize other electron sources in the process. In this instance, metabolic degradation of hydrocarbons is termed secondary utilization. Electron acceptors are elements or compounds that occur in relatively oxidized states. The more important electron acceptors are discussed in greater detail below.

In most subsurface environments, aerobic and anaerobic biodegradation can take place often in different parts of the same plume. From a thermodynamic perspective, microorganisms preferentially use electron acceptors that will provide the most free energy during respiration. Energy produced by the reactions is termed Gibb's Free Energy (ΔG_r). Negative values of ΔG_r indicate that the reaction is exothermic, i.e. produces energy, and therefore reactions shown in Figure 2-5 will proceed from left to right as written. To derive energy for cell maintenance and production, microorganisms must couple an endothermic reaction with an exothermic reaction resulting in a net gain in energy (i.e. $\Delta G_r < 0$). Table 2-3 illustrates the expected sequence for benzene oxidation of microbiologically mediated reactions based on the Gibb's Free Energy of the reaction (Wiedermeier et al., 1995). Although denitrification yields a higher Gibb's Free energy than aerobic respiration, free dissolved oxygen can be toxic to some anaerobic microorganisms at concentrations above 0.5 mg/L (Wiedermeier et al., 1995). Therefore, dissolved oxygen must be removed from groundwater before denitrification can occur.

Table 2-3. Expected Sequence of Microbially Mediated Benzene Oxidation Reactions and Their Gibb's Free Energy (ΔGr) (after Wiedermeier et al., 1995).

Process	ΔG_r (kJ/mol)
Aerobic Respiration	-3202
⇓	
Denitrification	-3245
⇓	
Iron (III) reduction	-2343
⇓	
Sulphate reduction	-514
⇓	
Methanogenesis	-136

The expected sequence of redox processes is also a function of the oxidizing potential of groundwater termed Eh^o. High Eh^o, also expressed as pE, means that groundwater has a relatively high oxidizing potential and will easily facilitate the transfer of electrons. As reduction of each oxidized species in the sequence occurs, microorganisms are forced to use electron acceptors with lower oxidizing capacity. This process can only continue as long as microorganisms can utilize compounds or redox couples that have a higher oxidizing potential than the contaminant of concern.

Naturally occurring mechanisms of attenuation for metals in the environment are important for understanding and remediating sites contaminated by heavy metals. For example, algal surfaces and exopolymers provide a complex array of potential adsorption sites, including electrostatic bonding for alkali earth metals, and redox reactions with noble metals (Lawrence et al., 1998). They noted that the presence of an exopolymer matrix surrounding the cell might also contribute to the immobilization of dissolved metals species through the provision of ion exchange sites. These sites may provide nucleation sites for mineral formation. Xue et al., (1988) noted that the algal cell surface presents carboxylic, amino, thio, hydroxo, and hydroxo-carboxylic groups that can be involved in the adsorption of heavy metals at the cell surface.

2.3.1 TYPES OF PROCESSES

2.3.1.1 Aerobic Biodegradation

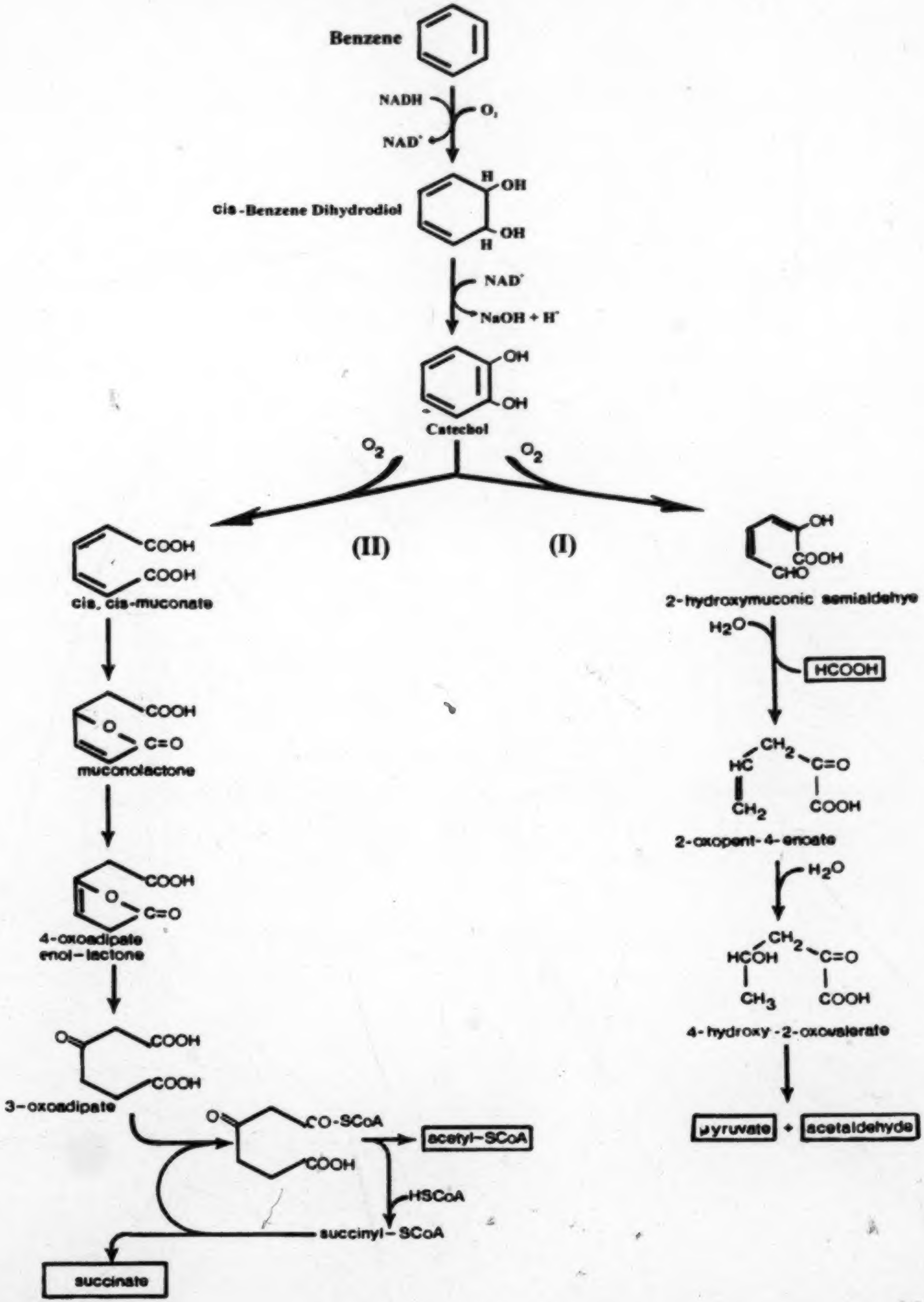
When native microorganisms are supplied with the necessary oxygen and nutrients to utilize contaminants as an energy source, biodegradation of the contaminants can occur via aerobic processes. Native populations of microorganisms have an advantage over introduced populations in that they are acclimated to the physical and chemical conditions in the subsurface. Aerobic attack on petroleum hydrocarbons requires the action of oxygenases and hence the presence of free oxygen in the subsurface. When high concentrations of organic or other contaminants are present, oxygen levels can quickly become depleted. This suggests that oxygen levels and not nutrient levels may be the most important limiting factor to aerobic biodegradation (Wiedermeier et al., 1995).

Low molecular weight hydrocarbons like BTEX can be readily biodegraded. Aromatic biodegradation involves the formation of a diol followed by cleavage and formation of a diacid. This is followed by ortho and meta cleavage of the ring structure (Smith, 1990). Figure 2-6 shows the ortho and meta cleavage biodegradative routes of benzene. During ortho cleavage, a dioxygenase enzyme cleaves between the two hydroxyl groups of catechol to produce *cis*, *cis*-muconate. This compound eventually degrades to succinic acid (Schneider and Billingsley, 1990). During meta cleavage of benzene, a dioxygenase enzyme cleaves adjacent to the hydrxyl groups. This leads to the formation of a semialdehyde (Schneider and Billingsley, 1990).

Biodegradation of n-alkanes (up to 22 Carbon atoms) begins with attack on the last or second to last carbon on the saturated chain and results in formation of a primary or secondary alcohol (Wiedermeier et al., 1995). The process continues, forming aldehydes, fatty acids, esters and ketones. Branched alkanes and cycloaliphatic compounds are difficult to degrade either because chains comprised of methyl or higher numbers of carbons can block the oxidation process or they require the presence of more than one bacteria type to provide the hydrogenases necessary for chain breakdown. Under aerobic conditions, less oxidized chlorinated aliphatic hydrocarbons, like dichloroethanes and vinyl chloride, can also act as the principal substrate and undergo oxidation-reduction reactions. In this type of reaction, the facilitating microorganisms obtain energy and organic carbon from degraded chlorinated aliphatic hydrocarbons (USEPA, 1998). In oxidation-reduction reactions, only the least oxidized chlorinated aliphatic hydrocarbon can be used as the electron acceptor.

Of the chlorinated ethenes, vinyl chloride is most susceptible to aerobic biodegradation and tetrachloroethene the least (USEPA, 1998). This is because highly chlorinated compounds tend to be much more oxidized than many compounds present in a natural groundwater system. Hartmans and de Bont (1992) showed that vinyl chloride can be used as a primary substrate under aerobic conditions, with end products, from direct mineralization of the vinyl chloride, being carbon dioxide and water. McCarty and

Figure 2-6. Biodegradative Routes of Benzene. (I) meta-Cleavage Route. (II) ortho-Cleavage Route (after Smith, 1990).



Benzene
NADH
O2
NAD+
cis-Benzene Dihydrodiol
H
OH
OH
H
NAD+
NaOH + H+
OH
OH
Catechol
O2
O2
(II)
(I)
COOH
COOH
cis, cis-muconate
COOH
O
C=O
muconolactone
COOH
O
C=O
4-oxoadipate enol-lactone
O
COOH
COOH
3-oxoadipate
O
CO-SCoA
COOH
acetyl-SCoA
HSCoA
succinyl-SCoA
succinate
OH
COOH
CHO
2-hydroxymuconic semialdehye
H2O
HCOOH
CH2
HC
C=O
CH2
COOH
2-oxopent-4-enoate
H2O
CH2
HCOH
C=O
CH3
COOH
4-hydroxy-2-oxovalerate
pyruvate
+
acetaldehyde

Semprini (1994) also showed that vinyl chloride and 1,2-dichloroethane could be used as the principal substrate in oxidation-reduction reactions under aerobic conditions.

Of the chlorinated ethanes, only 1,2-dichloroethane has been aerobically mineralized/oxidized (USEPA, 1998). In this case, the compound was transformed to chloroethanol, which was then transformed to carbon dioxide. Chlorinated benzenes with up to four chlorine atoms have also been readily biodegradable under aerobic conditions. Spain (1996) demonstrated that bacteria responsible for biodegradation were able to derive their carbon and energy from chlorobenzene degradation insitu. Daniel and Borden (1997) demonstrated that methyl tertiary butyl ether (MTBE) could be degraded under aerobic conditions. Limited degradation occurred near the MTBE source with no apparent evidence of degradation further downgradient.

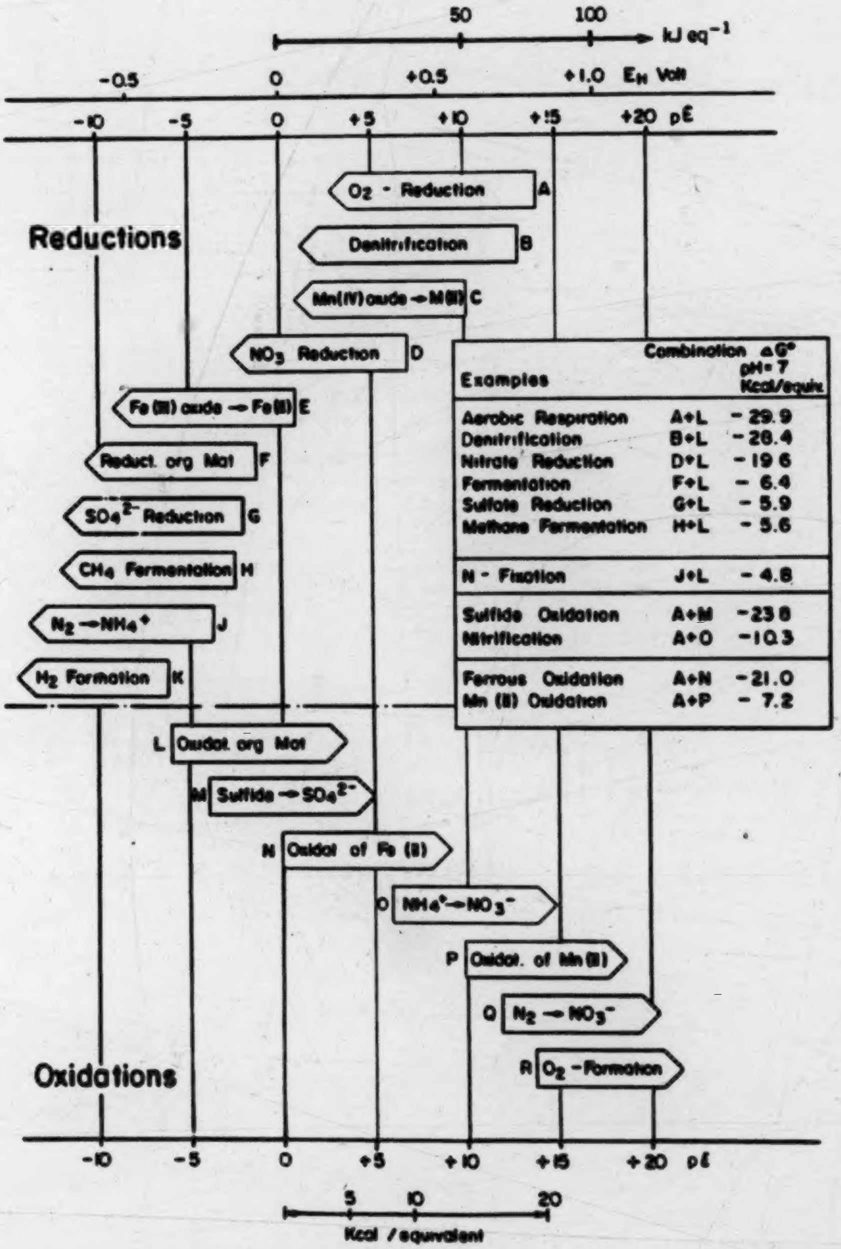
2.3.1.2 Anaerobic Biodegradation

Anaerobic biodegradation is initiated when oxygen levels become depleted within a dissolved contaminant plume or levels are lowered to the point where they do not effectively maintain aerobic microorganisms. Certain requirements must be met for anaerobic bacteria to begin to degrade contaminants: absence of dissolved oxygen in a plume, presence of bioavailable carbon sources, presence of electron acceptors and essential nutrients, and presence of proper ranges of contaminant concentrations, temperature, pH, salinity and redox potential. Under anaerobic conditions, iron (III), sulphate, nitrate, carbon dioxide, and manganese can act as electron acceptors.

During anaerobic biodegradation, aromatic compounds are first oxidized to phenols or organic acids, and then transformed to long-chain fatty acids. These compounds are then metabolized to carbon dioxide and possibly to methane.

Biodegradation of fuel hydrocarbons will occur via denitrification, manganese (IV) reduction, iron (III) reduction, sulphate reduction and methanogenesis. Figure 2-7 shows

Figure 2-7. Sequence of Microbially Mediated Redox Processes and Electron Acceptor Depletion (after Stumm and Morgan, 1996)


50
100
kJ eq^{-1}
-0.5
0
+0.5
+1.0
E_H Volt
-10
-5
0
+5
+10
+15
+20
pE
Reductions
O_2 - Reduction A
Denitrification B
Mn(IV) oxide → M(II) C
NO_3 Reduction D
Fe (III) oxide → Fe(II) E
Reduct. org Mat F
SO_4^{2-} Reduction G
CH_4 Fermentation H
$N_2 \rightarrow NH_4^+$ J
H_2 Formation K
L Oxidat. org Mat
M Sulfide → SO_4^{2-}
N Oxidat of Fe (II)
O $NH_4^+ \rightarrow NO_3^-$
P Oxidat. of Mn (II)
Q $N_2 \rightarrow NO_3^-$
R O_2 - Formation
Oxidations
-10
-5
0
+5
+10
+15
+20
pE
5
10
20
Kcal / equivalent

Examples	Combination	ΔG° pH = 7 Kcal/equiv.
Aerobic Respiration	A+L	- 29.9
Denitrification	B+L	- 28.4
Nitrate Reduction	D+L	- 19.6
Fermentation	F+L	- 6.4
Sulfate Reduction	G+L	- 5.9
Methane Fermentation	H+L	- 5.6
N - Fixation	J+L	- 4.8
Sulfide Oxidation	A+M	- 23.8
Nitrification	A+O	- 10.3
Ferrous Oxidation	A+N	- 21.0
Mn (II) Oxidation	A+P	- 7.2

the sequence of microbiologically mediated redox reactions, the redox potential that favours those reactions, and the depletion sequence of electron acceptors as reactions occur.

Polychlorinated ethenes are unlikely to undergo anaerobic oxidation due to their oxidized nature. However, Bradley and Chapelle (1996) showed that vinyl chloride can be directly oxidized to carbon dioxide via iron (III) reduction.

2.3.1.3 Denitrification

Denitrification can occur in a contaminant plume after the aerobic bacteria have utilized almost all of the dissolved oxygen. Starr and Gilham (1993) have identified four requirements for the occurrence of denitrification: presence of nitrate in the aquifer system, presence of available organic carbon, presence of denitrifying bacteria, and presence of reducing conditions.

Denitrification occurs in the following sequence:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (14)$$

Each of the reactions in this sequence is facilitated by a different microorganism (Chapelle, 1993). Therefore, a mixed population of microorganisms is required to complete the denitrification process. Denitrification is favoured under pH conditions ranging from 6.2 to 10.2.

2.3.1.4 Iron (III) Reduction

Iron (III) can be used as an electron receptor after available oxygen and nitrate are utilized. During iron (III) reduction, iron is reduced to iron (II). Quigley and Banwart (1999) discuss three mechanisms for iron (III) reduction: direct contact between cell and iron (III), transport of iron (III) to the cell, and electron shuttling. Bradley and Chapelle (1996) demonstrated evidence of mineralization of vinyl chloride under iron reducing conditions as long as a sufficient supply of bioavailable iron (III) was present in the contaminant plume. Gerlach et al., (1999) successfully demonstrated that chromium (VI) could be reduced to chromium (III) by exposing it to redox-reactive iron (II). In this case, introduced iron (III) was reduced by another bacterium. Chromium (III) precipitates (hydroxides of chromium and iron) are considered to be stable under most conditions assumed for a natural groundwater system.

2.3.1.5 Sulphate Reduction

Sulphate reduction occurs after available oxygen and nitrate have been utilized by aerobic microorganisms. However, sulphate reduction is not as thermodynamically favourable as iron (III) reduction. Sulphate reducing bacteria are sensitive to temperature, inorganic nutrients and pH. Landmeyer et al., (1998) demonstrated in field and lab studies that toluene, benzene and naphthalene could be degraded to CO_2 under anaerobic sulphate reducing conditions. Their observations were supported by high hydrogen sulphide concentrations and the presence of considerable levels of sulphate in groundwater associated with contamination at a former manufactured gas plant in South Carolina. Some iron (III) reduction of contaminants was also indicated by geochemical data from the site. Rügge et al., (1998) also noted significant reduction of toluene, o-xylene, and napthalene in an evaluation of the potential for natural attenuation in a landfill leachate plume.

Sulphide production by sulphate reducing bacteria as a result of biodegradation of organic contaminants can also be beneficial in the removal of metals in the subsurface. Many heavy metals such as mercury, cadmium, and copper form insoluble metal sulphides. These compounds have the lowest recorded solubilities as a sulphide solid (solubility product values in the 10^{-40} range, Eccles, 1998).

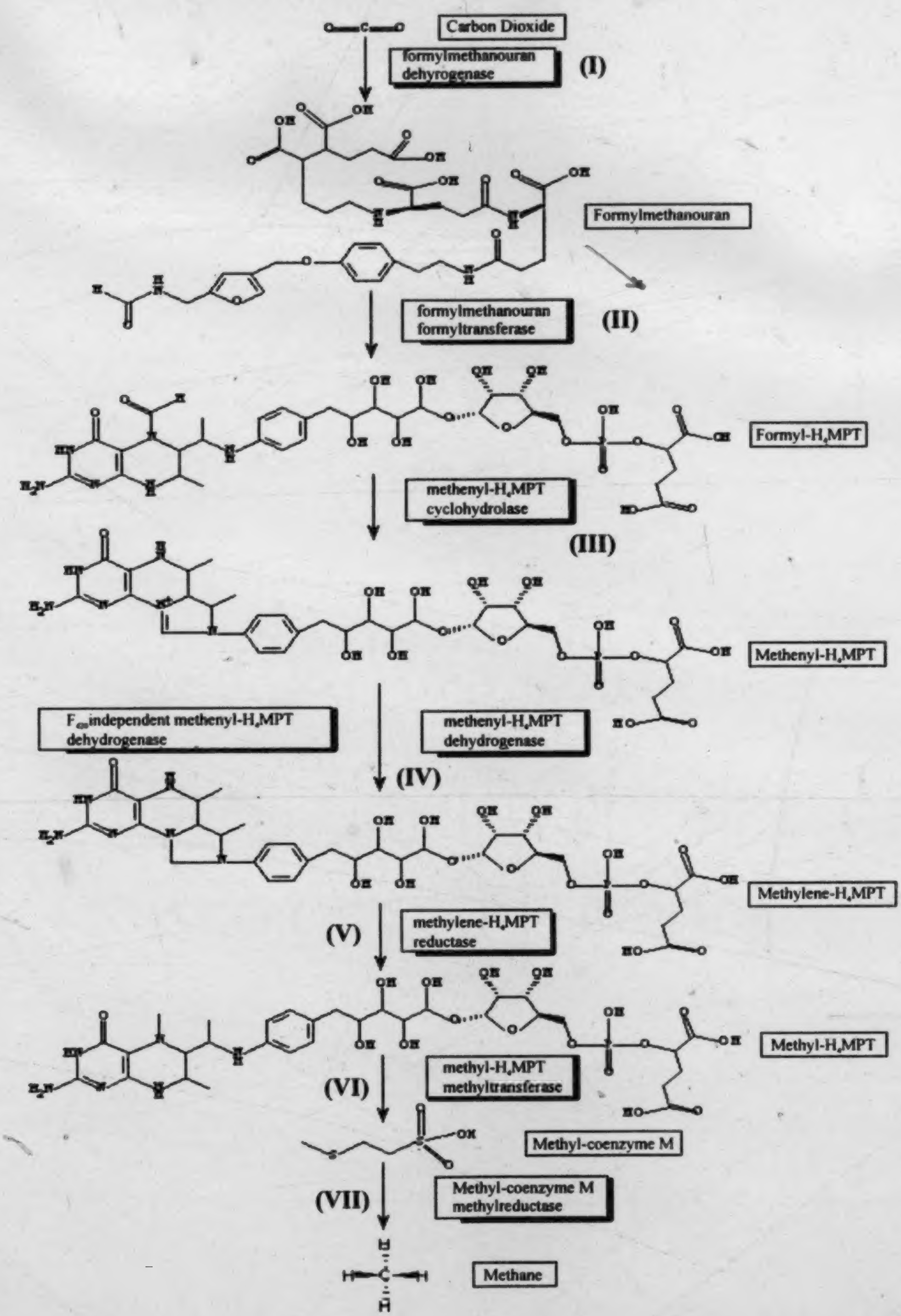
2.3.1.6 Methanogenesis

Once groundwater is sufficiently reducing, the CO_2-CH_4 redox couple can be used to oxidize fuel hydrocarbons. This is because the redox couple has the appropriate free energy yield and oxidizing potential. However, methanogenesis will only occur after other highly oxidizing species such as oxygen, nitrate, and manganese are utilized. Methanogenesis occurs in at least four steps (Chapelle, 1993). Figure 2-8 shows the steps involved in the methanogenesis pathway from carbon dioxide to methane and the enzymes involved in each step. In each step hydrogen reacts with a carbon. The reaction is facilitated by an enzyme. During the final step, a methyl-coenzyme-M-methylreductase (CoM-CH_3) complex is formed and the carbon is reduced to methane. Bradley and Chapelle (1997) demonstrated mineralization of DCE to carbon dioxide under methanogenic conditions.

Godsy et al., (1992) studied methanogenic biodegradation of creosote contaminants at an abandoned wood treatment facility in Florida. The water soluble fraction resulting from the disposal of process wastes was enriched in organic acids, phenols, single and double ringed polyaromatic hydrocarbons and single and double ringed nitrogen, oxygen and sulphur containing compounds. Pore water samples taken from within the plume indicated populations of methanogenic bacteria two orders of magnitude higher than background populations. Sampling results downgradient of the source area indicated a three-step sequential transformation or degradation of the contaminants in the following order: (1) quinoline, isoquinoline, benzoic acid, and $C_3 - C_6$ volatile fatty acids; (2) phenol; and (3) 2-,3-,4-methylphenol, 2(1H)-quinolinone, and 1(2H)-isoquinolinone (Godsy et al., 1992). End products of the biodegradation process were methane and carbon dioxide. Of special note was that degradation of the compounds took place at a pH of less than 6.

Westervelt et al., (1997) investigated the remediation of arctic diesel fuel at Fort Wainwright army base in Alaska. The spill at the army base occurred within 90 metres of two downgradient drinking water supply wells. Geochemical analysis indicated that

Figure 2-8. Steps Involved in Methanogenesis Pathway from Carbon Dioxide to Methane (after Ma, 1999).


Carbon Dioxide
formylmethanouran dehyrogenase
(I)
Formylmethanouran
formylmethanouran formyltransferase
(II)
Formyl-H$_4$MPT
methenyl-H$_4$MPT cyclohydrolase
(III)
Methenyl-H$_4$MPT
F$_{420}$-independent methenyl-H$_4$MPT dehydrogenase
methenyl-H$_4$MPT dehydrogenase
(IV)
Methylene-H$_4$MPT
(V)
methylene-H$_4$MPT reductase
Methyl-H$_4$MPT
(VI)
methyl-H$_4$MPT methyltransferase
Methyl-coenzyme M
(VII)
Methyl-coenzyme M methylreductase
Methane

the fuel was undergoing anaerobic biodegradation by a number of pathways. However, methanogenesis was the dominant pathway. Transport modeling indicated that all of the contaminated groundwater would be captured by the supply wells. However, groundwater monitoring results indicated that contamination was reduced to non-detectable levels within 45 metres of the source area.

2.3.1.7 Reductive Dechlorination

The most important process in natural biodegradation of more highly chlorinated solvents is reductive dechlorination (USEPA, 1998). During this process, the chlorinated hydrocarbon becomes the electron acceptor, not a source of carbon, and a chlorine atom is removed and replaced with a hydrogen atom. In general, reductive dechlorination of tetrachloroethene (PCE) progresses from PCE to trichloroethene (TCE) to dichloroethene (DCE, of which there are three isomers) to vinyl chloride to ethene. In theory it is possible for all three isomers of DCE to be produced during the reductive dechlorination process. However, Bouwer (1994) reports that *cis*–1,2-DCE is a more common daughter product than *trans*-1,2-DCE and that 1,1-DCE is the least common daughter product when the parent product is biodegraded. Therefore, reductive dechlorination is characterized by buildup of daughter products and an increase in chloride ion concentration in the plume. PCE is the ethene most susceptible to reductive dechlorination whereas vinyl chloride is the least susceptible as it is the least oxidized of the ethenes. Therefore, over the course of reductive dechlorination for ethene, the rate of dechlorination decreases with the progression of the process. Reductive dechlorination has been demonstrated under nitrate and iron reducing conditions. However, Bouwer (1994) reports that the most rapid biodegradation rates, affecting the widest range of chlorinated aliphatic hydrocarbons, occurs under sulphate reducing or methanogenic conditions. Because a chlorinated hydrocarbon is used as the electron acceptor, there must be an alternate bioavailable carbon source of sufficient quantity for microorganism growth and maintenance. Sources could include fuel hydrocarbons or natural organic matter.

Reductive dechlorination of tetrachloroethene and carbon tetrachloride was reported by Hardy et al., (1999) at a former chlorinated solvent manufacturing site in Brazil. One form of bacteria utilized 1,2-dichloropropane as the electron donor and the chlorinated solvents as electron acceptors. The 1,2-dichloropropane was oxidized by iron (III) and manganese reducing bacteria.

Dechlorination of tetrachloroethene and trichloroethene to dichloroethene is favoured under mildly reducing conditions such as nitrate or iron (III) reduction, whereas transformations of dichloroethene to vinyl chloride or vinyl chloride to ethylene require the more strongly reducing conditions of methanogenesis (DiStefano et al., 1991). Patterns of molecular hydrogen concentrations in a contaminant plume have been shown by Chapelle (1996) to provide a reliable delineation of the different reducing zones within a plume. Pfiffner et al., (1999) also report that redox conditions, (aquifer) media composition, and electron acceptors and donors influence the effectiveness of natural attenuation of chlorinated solvents.

2.3.1.8 Cometabolism

During cometabolism of a chlorinated aliphatic hydrocarbon, degradation is catalyzed by an enzyme or cofactor that is fortuitously produced by the organisms for other purposes (USEPA, 1998). The organisms do not seem to derive any benefit from cometabolism and may in fact be harmed by the process (McCarty and Semprini, 1994). The best documentation for cometabolism at a site indicates that the process involves catabolic oxygenases that catalyze the initial step in oxidation of their respective primary or growth substrate (e.g. BTEX or other organic compounds) under aerobic conditions (USEPA, 1998). McCarty and Semprini (1994) reported that under aerobic conditions, chlorinated ethenes, with the exception of PCE, are susceptible to cometabolic biodegradation. However, Tartakovsky et al., (1997) indicate that PCE can undergo cometabolism by aerobic methanotrophic bacteria. Bacteria use an enzyme called soluble methane monooxygenase to oxidize methane. This enzyme has broad substrate specificity and oxidizes a wide range of chlorinated compounds.

McCarty and Semprini (1994) also report that chlorinated ethenes can undergo cometabolism in aerobic conditions. Aerobic cometabolism of the ethenes may be characterized by a loss of contaminant mass, presence of intermediate degradation products such as chlorinated oxides, aldehydes, ethanols, or epoxides, and the presence of other products such as chloride, carbon dioxide, carbon monoxide, and organic acids.

2.3.2 ELECTRON DONORS/ACCEPTORS

2.3.2.1 Dissolved Oxygen

Dissolved oxygen is the most thermodynamically favoured electron acceptor used in the biodegradation of fuel hydrocarbons (Wiedermeier et al., 1995). Dissolved oxygen concentrations in groundwater are used to estimate the potential mass of a contaminant that can be biodegraded by aerobic processes. It is estimated that for each 1.0 mg/L of dissolved oxygen present in groundwater and consumed by the microorganisms, 0.32 mg/L of BTEX (benzene, toluene, ethylbenzene, and xylene respectively) will be oxidized and destroyed (Wiedermeier et al., 1995). As hydrocarbons are consumed, the level of dissolved oxygen drops. Hence, inside the contaminant plume, the level of dissolved oxygen is expected to be lower than the level outside the plume if aerobic biodegradation is occurring. As a rule, anaerobic microorganisms cannot function at dissolved oxygen concentrations above 0.5 mg/L.

Dissolved oxygen levels in a monitoring well can be measured either in the lab or in the field. Samples can be collected from the well either with a dedicated low volume pump or with a disposable bailer. A low volume pump is preferred so that the sample does not become aerated when extracted. Readings should be taken before and after purging as a check on the efficiency of sample extraction.

2.3.2.2 Nitrate

Once dissolved oxygen has been depleted, nitrate may be used by nitrate reducing bacteria as an electron acceptor for anaerobic biodegradation via denitrification. Dissolved nitrate levels in groundwater are used to estimate the potential mass of contaminant that can be biodegraded via denitrification. Comparisons between nitrate levels in a plume and background nitrate levels when combined with the estimated volume of contaminated groundwater allow for an estimation of the amount of fuel hydrocarbons (BTEX) lost due to denitrification. Chapelle (1993) provides evidence that benzene can be biodegraded under nitrate reducing conditions. Each 1.0 mg/L of ionic nitrate consumed by microorganisms results in the destruction of approximately 0.21 mg/L of BTEX (Wiedermeier et al., 1995).

Soil column studies on the degradation of trinitrotoluene (TNT) by Cattaneo et al., (1997) indicated that organic carbon present in soil was sufficient to promote conversion of TNT into amino-intermediates. A decrease in nitrate levels from 149 mg/L at the top of the column to non-detectable levels at the bottom of the column was seen as evidence that denitrification was a process responsible for removal of TNT from the soil column.

2.3.2.3 Iron

Dissolved iron (III) is sometimes used as an electron acceptor during anaerobic biodegradation of BTEX. The biodegradation process results in the reduction of iron from iron (III) to iron (II), which may be soluble in groundwater. Sampling and analysis for iron (II) can therefore provide an indication of anaerobic biodegradation of BTEX. Quigley and Banwart (1999) report that the form of iron (III) is critical to its bioavailability and therefore its contribution to biodegradation. Microorganisms readily metabolize poorly crystalline iron (III) but not the less reactive, more crystalline forms. Soluble and chelated forms of iron (III) are reduced the fastest. The presence of suitable chelating ligands has been found to dramatically increase the rates of biodegradation of aromatic hydrocarbons coupled to iron (III) reduction (Quigley and Banwart, 1999).

Estimates of the mass of BTEX destroyed by iron (III) reduction are made by knowing the volume of contaminated groundwater, the concentration of iron (II) in the plume and the background concentration of iron (II). The biodegradation of 1.0 mg/L BTEX results in the production of 21.8 mg/L iron (II) during iron (III) reduction (Wiedermeier et al., 1995).

2.3.2.4 Sulphate

Sulphate may be used by sulphate-reducing bacteria as an electron acceptor during anaerobic biodegradation of fuel hydrocarbons after available dissolved oxygen, nitrate, and iron (III) have been depleted in a contaminant plume. BTEX biodegradation results in a reduction of sulphate to sulphide (Wiedermeier et al., 1995). In general, the extent and significance of BTEX biodegradation via sulphate reduction is not well understood (Norris et al., 1994). A study by Jobson et al., (1979) indicated that sulphate-reducing bacteria only grew on the residues of aerobic bacterial degradation of some hydrocarbons. Lammey and Noseworthy (1997) undertook a study of intrinsic biodegradation processes occurring in association with a diesel and aviation gas spill at Canadian Forces Base Goose Bay in Labrador. They found that both aerobic respiration and anaerobic bioremediation (particularly sulphate reduction, iron (III) reduction, and denitrification) were occurring within the contaminant plume. These processes were effective even at a groundwater temperature of 5°C. Wiedermeier et al., (1995) suggests that estimates of the mass of BTEX destroyed by sulphate reduction can be are made by using the volume of contaminated groundwater, the concentration of sulphate in the plume, and the background concentration of sulphate. They indicate that for each 1.0 mg/L of sulphate consumed by microorganisms results in the destruction of approximately 0.21 mg/L of BTEX.

2.3.2.5 Manganese

Manganese is sometimes used as an electron acceptor during biodegradation of fuel hydrocarbons. The degradation process results in reduction of manganese (IV) to manganese (II). In anaerobic groundwater contaminated with BTEX and a source of manganese (IV), manganese (II) can be used as an indicator of biodegradation. Cozzarelli et al., (1990) studied biodegradation of crude oil at a site in Minnesota. They determined that the major reaction pathways in biodegradation of organic matter involved manganese and iron reduction as well as methanogenesis. Near the crude oil zone, the reducing chemical environment was characterized by high concentrations of carbon dioxide, manganese, iron, and methane.

Anaerobic biodegradation studies on sulfolane and diisopropanolamine (DIPA) by Fedorak et al., (1997) indicated that DIPA could be degraded by manganese reduction, iron (III) reduction and denitrification. These studies were carried out on aquifer sediments from Alberta at temperatures of 8°C and 28°C. Significant degradation was noted at 8°C but not at 28°C.

2.3.2.6 Methane, Carbon Dioxide and Acetate

Methane is produced as a byproduct of anaerobic biodegradation of fuel hydrocarbons using carbon dioxide or acetate as the electron acceptor (Chapelle, 1993). This process usually occurs after concentrations of dissolved oxygen, nitrate, bioavailable iron III and sulphate are depleted in a contaminant plume. Presence of methane in a plume above background levels is an indicator of strongly reducing conditions because methane is not found in fuel hydrocarbons. Estimates of the mass of BTEX destroyed by methanogenesis are made by using the volume of contaminated groundwater, the concentration of methane in the plume and the background concentration of methane. The biodegradation of 1 mg/L of BTEX results in the production of approximately 0.78 mg/L of methane during methanogenesis (Wiedermeier et al., 1995).

2.3.3 OTHER GEOCHEMICAL INDICATORS AND PARAMETERS ASSOCIATED WITH BIODEGRADATION

2.3.3.1 Alkalinity

The total alkalinity of a groundwater system is an indication of a water's capacity to neutralize acid (Stumm and Morgan, 1996). Alkalinity in groundwater results from the presence of carbonates, hydroxides and bicarbonates of elements such as calcium, magnesium, sodium, potassium or ammonia. These species occur due to dissolution of rocks, particularly carbonates, transfer of carbon dioxide from atmosphere via recharge to a groundwater system, and respiration of microorganisms in the subsurface. During biodegradation, alkalinity prevents lowering of groundwater pH as a result of the introduction of acids generated by aerobic and anaerobic processes such as denitrification and sulphate reduction. Alkalinity plays an important role in the success of biodegradation of fuel hydrocarbons by maintaining pH of a groundwater system.

As a rule, areas contaminated by fuel hydrocarbons have higher concentrations of total alkalinity than background areas. This is because chemical reactions involved in biodegradation of hydrocarbons cause an increase in alkalinity of a groundwater system due to respiration of the microorganisms. Volatile fatty acid utilization by microorganisms also produces bicarbonate, which is a component of alkalinity. Changes in alkalinity are more pronounced during aerobic biodegradation, denitrification, iron reduction, and sulphate reduction and less pronounced during methanogenesis (Morel and Hering, 1993). Each 1.0 mg/L of alkalinity produced by microorganisms results from the destruction of approximately 0.13 mg/L of total BTEX (Wiedermeier et al., 1995).

2.3.3.2 Oxidation/Reduction Potential (Eh^{o})

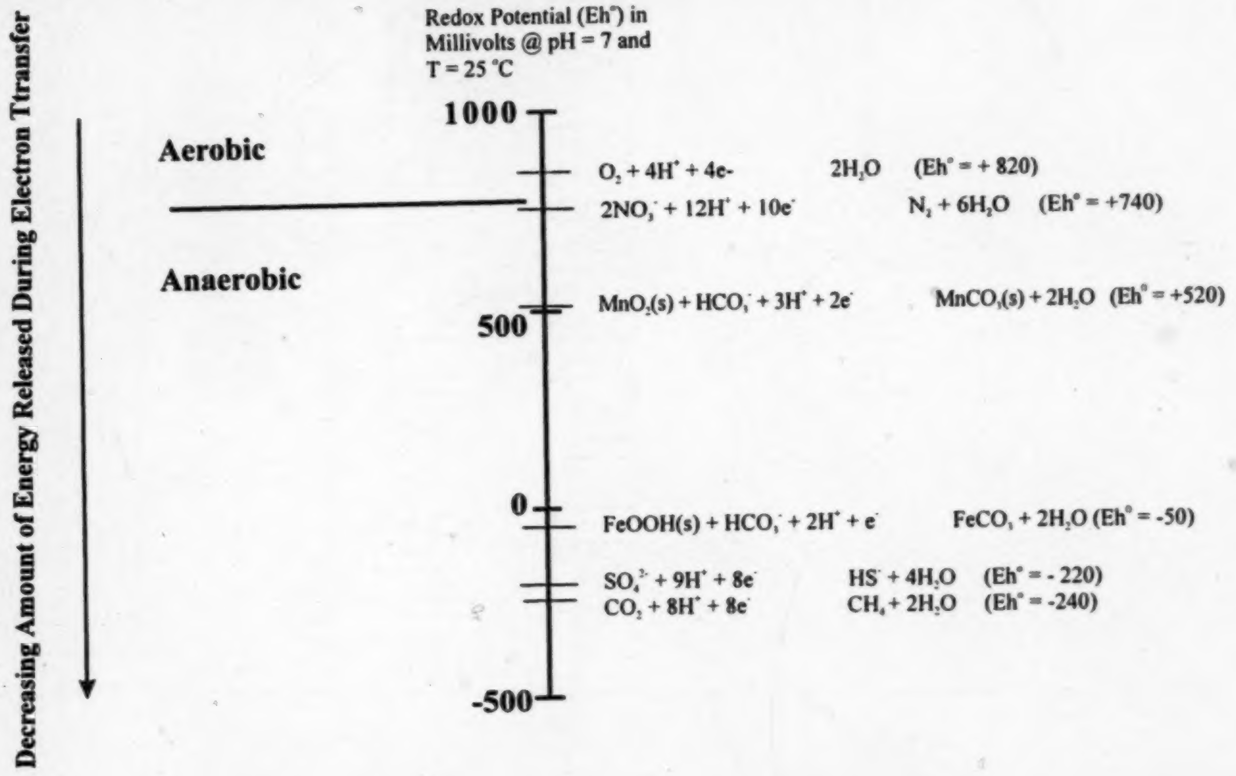
The oxidation/reduction potential of a groundwater system provides an indication of the tendency of groundwater to accept or transfer electrons. Reactions involving oxidation/reduction (redox) of fuel hydrocarbons in groundwater are usually facilitated biologically. Therefore, redox potential of a groundwater system depends upon and influences rates of biodegradation. Some biological processes operate only within a set range of redox conditions making knowledge of redox potential of a groundwater system important. Figure 2-9 shows typical redox conditions for the more common biodegradation processes.

Redox potential can also be used in the field and during data analysis to determine the approximate location of the contaminant plume. Analytical results for redox are influenced by aeration of the sample during collection. Therefore, care must be taken to minimize potential aeration during sampling.

2.3.3.3 Temperature, pH, and Conductivity

Temperature of a groundwater system can affect solubility of dissolved oxygen and other geochemical species. Dissolved oxygen is more volatile in warmer groundwater. Groundwater temperature also affects bioactivity of microorganisms. Rates of hydrocarbon biodegradation roughly double for every 10°C increase in temperature over the temperature range between 5°C and 25°C (Wiedermeier et al., 1995). Groundwater temperatures less than 5°C are thought to inhibit biodegradation or slow rates of biodegradation. However, Herrington et al., (1997) showed that significant biodegradation rates could still be achieved at sites in Alaska where groundwater temperatures were consistently below 10 °C. To study differences in toluene degradation at temperate versus cold climates, Bradley and Chapelle (1995) compared rates of degradation for a defined microbiological community at sites in Adak, Alaska and Hanahan, South Carolina. In Adak, groundwater temperatures were around 5°C while in Hanahan, groundwater temperatures were around 20°C. They found that rates of toluene degradation in Adak were higher than those in Hanahan (16.3 percent of total toluene per day and 5.1 percent per day, respectively). In addition, rates of overall microbiological metabolism in sediments from the two sites, as estimated by acetate mineralization, were similar (~10.6% day^{-1}) at their respective insitu temperatures. This

Figure 2-9. Redox Potentials for Various Electron Acceptors (after Norris et al., 1994)


Decreasing Amount of Energy Released During Electron Ttransfer
Redox Potential (Eh°) in Millivolts @ pH = 7 and T = 25 °C
1000
500
0
-500
Aerobic
Anaerobic
$O_2 + 4H^+ + 4e-$ $2H_2O$ (Eh° = + 820)
$2NO_3^- + 12H^+ + 10e^-$ $N_2 + 6H_2O$ (Eh° = +740)
$MnO_2(s) + HCO_3^- + 3H^+ + 2e^-$ $MnCO_3(s) + 2H_2O$ (Eh° = +520)
$FeOOH(s) + HCO_3^- + 2H^+ + e^-$ $FeCO_3 + 2H_2O$ (Eh° = -50)
$SO_4^{2-} + 9H^+ + 8e^-$ $HS^- + 4H_2O$ (Eh° = - 220)
$CO_2 + 8H^+ + 8e^-$ $CH_4 + 2H_2O$ (Eh° = -240)

provides support to the concept that microbiological populations can adapt to colder climates and provide high rates of growth and metabolism under colder temperatures.

The pH of groundwater can affect the presence and activity of microbiological populations. This is especially true of methanogens. Microorganisms capable of biodegrading fuel hydrocarbons generally prefer a pH range of 6 to 8.

Conductivity is a measure of the ability of a solution to conduct electricity. Groundwater conductivity is directly related to the concentration of ions in solution and increases with increased ion concentration. Conductivity measurements can be used as a check to ensure that groundwater samples collected during site characterization and monitoring are representative of groundwater in the same saturated zone as that of the contaminant plume. If conductivities of the plume and the samples are radically different, they may be from different zones and additional monitoring locations in the proper zone are required.

2.3.3.4 Chloride

Chloride can be used in the same way as conductivity to ensure that the proper saturated zone is being monitored and sampled. Elevated chloride levels within a contaminant plume as compared to background may be an indication that reductive dechlorination of chlorinated solvents is occurring. Isotope ratios of chloride can be used to provide evidence that in situ bioremediation is occurring in situations where chemical measurements alone may not provide sufficient or conclusive evidence. Sturchio et al., (1998) investigated changes in ^{37}Cl isotope ratios between the parent compound trichloroethene and its degradation products. Groundwater samples were taken from wells at a gaseous diffusion plant in Kentucky. They found that the ^{37}Cl isotope values for trichloroethene increased with its decreasing concentration in groundwater. Each successive degradation product had lower ^{37}Cl isotope values.

2.3.3.5 Field Dehydrogenase Test

The field dehydrogenase test is a qualitative method used to determine if aerobic bacteria are present in an aquifer in quantities capable of biodegrading fuel hydrocarbons (Wiedermeier et al., 1995). If the test gives a positive result, a sufficient number of microorganisms capable of aerobic metabolism and/or denitrification are present in the groundwater system. No differentiation of process is available with this test. In addition, the test gives no indication of the presence of facultative anaerobic microorganisms in the groundwater system.

2.3.3.6 Volatile Fatty Acids

Volatile fatty acids are produced during biodegradation of BTEX compounds. The presence of volatile fatty acids in a contaminant plume is a direct indication that biodegradation of BTEX has occurred. Individual organic acid concentration can also provide an indication of biodegradation (Seagren and Becker, 1999). Their research determined that under methanogenic conditions, degradation of petroleum hydrocarbons produced a ratio of acetate to benzoate that was greater than that for sulphate-reducing conditions.

2.3.3.7 Hydrogen Gas

Dissolved hydrogen gas is produced in anaerobic groundwater systems where natural and man-made organic matter is decomposed by fermentative microorganisms. The hydrogen gas is then consumed by microorganisms that use nitrate, iron (III), sulphate, or carbon dioxide as electron acceptors. In effect, hydrogen is continuously cycled between microorganism species. The different electron acceptor reducing microorganisms have different efficiencies in utilizing available hydrogen. Nitrate reducers are highly efficient hydrogen users whereas methanogenic bacteria are less efficient users. Primary and secondary fermentation reactions generally produce hydrogen used in reductive dechlorination of chlorinated solvents. For dechlorination to occur, hydrogen respirators must compete successfully against other hydrogen utilizers for the available hydrogen (Wiedermeier et al., 1999). This difference in hydrogen use is reflected in the subsurface hydrogen concentration and can be a means of identifying which electron accepting process is responsible for degradation of a contaminant.

2.3.3.8 Carbon Isotopes

Two isotopes of carbon, C^{12} and C^{13}, can be used to evaluate natural attenuation of organic contaminants. The ratio of C^{12} to C^{13} can be changed by chemical reactions and this ratio provides information regarding the type of biodegradation process in the subsurface. For example, Revesz et al., (1995) studied carbon and hydrogen isotope ratios in methane produced at a crude oil spill in Minnesota. They found that C^{13} measurements could provide accurate information on the source of methane production and the biodegradation processes involved. Theoretically, stable carbon isotope ratios would be able to save analytical costs due to the cost for their analysis being cheaper than that for actual contaminants and the potential for fewer analyses per site during post implementation monitoring of the site. However, greater initial site characterization is required in order to understand background isotope conditions. In addition, stable isotope analysis does not provide confirmation of contaminant mass or concentration reduction. Rather, it only gives an indication of the processes involved. This information, together with rate studies may satisfy regulators that reduction will occur rather than directly measuring that reduction.

2.3.3.9 K_d Values

Brady et al., (1998) discuss the use of K_d values (solid/fluid distribution coefficients) to demonstrate irreversible metals adsorption. They suggest that if irreversible adsorption has occurred, the K_d value should increase with time and be greater at the source of the plume than at the leading edge of the plume. Groundwater samples could be collected along the axis of the plume and near the source over time to evaluate this method. If K_d's increase with time, it could be argued that irreversible adsorption is occurring. They further suggest that steepness of the K_d versus distance curve might be used to predict how long the metals remain in solution, thereby giving a prediction of the duration for natural attenuation to be effective at a site.

2.3.4 MICROCOSM STUDIES

Some protocols for determining the applicability of natural attenuation as a remediation option require microcosm studies as a tertiary line of evidence after historical and geochemical data review. Microcosm studies are lab or field evaluations of microorganism populations and the processes utilized by those populations in degrading a contaminant. Microcosm studies are undertaken to show that microorganisms necessary for biodegradation of contaminants are present in the area of contamination. Microcosm studies can be strongly influenced by geological material submitted for study, physical properties of the microcosm, sampling strategy, and duration of the study.
Microcosm studies are appropriate for indicating the potential for insitu biodegradation and as proof that losses of contaminants are biological in origin. They may also be used to provide a quick indication that contaminants are being biodegraded. For example, an increase in microbiological population size within a contaminant plume versus background population levels may be an indication that degradation is occurring. However, microcosm studies should be used with caution to calculate biodegradation rate constants. This is because rate constants calculated from a microcosm study are generally higher than those realized in the field (Suarez and Rifai, 1999). In the lab, it is easier to maintain ideal ambient conditions for biodegradation.

Schroth et al., (1997) suggest that there are some inherent problems with conducting microcosm studies and that site specific information is required to better quantify microbiological metabolic activities. Problems discussed include the need for core material, difficulty in reproducing field conditions in the lab (potentially resulting in preferential bacteria growth), and inability to compute mass balances for reactants and products. Therefore, biodegradation rate constants should be calculated from field measurements.

Microcosm studies can be used to identify potential intermediate compounds associated with a particular degradation process. This information can be used when developing a monitoring program for a site so that intermediates can be monitored for confirmation that degradation is taking place.

Microcosm studies can also be used to determine types of processes affecting contaminants. Landmeyer et al., (1998) determined that benzene, toluene, and naphthalene could undergo both aerobic and anaerobic biodegradation by evaluating degradation processes with microcosm studies.

There are several types of basic microcosm studies that can be conducted for a site. Total heterotrophic plate counts (aerobic or anaerobic) indicate the total number of bacteria that can grow on a wide variety of carbon/energy sources (Hinchee et al., 1995). A most probable number (MPN) study indicates population numbers of specific groups of anaerobes such as iron or sulphate reducers or methanogens. Direct counts use microscopy to more accurately determine total bacteria in a sample. While bacteria counts provide an indication that bacteria are present, they do not necessarily indicate that the bacteria can biodegrade contaminants of concern. In contrast, contaminant specific bioassays provide direct evidence of populations of contaminant degrading bacteria at a site. Assays can provide bacteria counts for specific contaminants or families of contaminants. Volatile fatty acid analyses and genetic probes are examples of more advanced genetic and biochemical methods that can be used to characterize specific contamination degradation activities.

2.3.5 NATURAL ATTENUATION RATE STUDIES

Biodegradation rates are sometimes calculated to provide an estimate of the length of time required to remediate a contaminated site or to predict contaminant plume lengths. Existing protocols for natural attenuation require documentation of three lines of evidence to support the occurrence of natural attenuation. The biodegradation rate can be used as support for the first line of evidence which is the loss of contaminants. Wiedermeier et al., (1996) used two different methods to determine the biodegradation rate constant for BTEX in groundwater at Hill Air Force Base in Utah. The first method involved use of a biologically recalcitrant tracer, trimethylbenzene that was introduced into groundwater at the source of the BTEX contamination. This compound was selected because its three isomers have Henry's Law constants and soil sorption coefficients similar to those of BTEX. Rates of tracer loss versus hydrocarbon loss at downgradient monitoring points were compared. Attenuation of the tracer was attributed to physical and chemical processes. Attenuation in excess of that of the tracer was attributed to biodegradation. The second method involved modeling of the analytical data using a one-dimensional analytical solution derived by Buscheck and Alcantar. The solution assumes a steady state for the plume and that effects from sorption, dispersion, and volatilization are negligible. Wiedermeier et al., (1996) were able to calculate first order rate constants from their study that were similar for both methods. However, the second method was sensitive to rate of dispersivity selected for the site. Therefore, site specific data would provide the best estimate of biodegradation rate.

Degradation rate studies can also be used to determine the types of processes affecting contaminants and which processes may be more effective at degrading contaminants of concern. Studies conducted by Landmeyer et al., (1998) indicated effective rate constants for benzene, toluene, and naphthalene under both aerobic and anaerobic conditions. However, aerobic rate constants were much higher (two to three orders of magnitude) than anaerobic rate constants.

2.3.6 BIODEGRADATION INTERMEDIATES

Biodegradation intermediates are compounds formed during the biodegradation process. In the discussion of different biodegradation processes and types of contaminants that can be biodegraded, several metabolites have already been mentioned. For example, phenol is an intermediate of benzene biodegradation under methanogenic conditions. Ethene is a metabolite of chlorinated solvents such as tetrachloroethene, trichloroethene, or vinyl chloride which undergo reductive dechlorination. Chloride can also be released during this process. Vinyl chloride itself is a metabolite of chlorinated solvents under certain degradation processes. Godsy et al., (1992) found that acetate was an intermediate in methanogenic biodegradation of the water-soluble fraction of creosote contaminants.

The concern with intermediates is that they may be more toxic and mobile than the parent compound. For example, vinyl chloride is a carcinogen whereas dichloroethene is not. In this case, a monitoring program must be able to detect and delineate the extent of these intermediates and ensure that they are also being attenuated and do not become a potential threat to receptors or to the existing microbiological population.

Table 2-4, adapted from Cozzarelli et al., (1990), shows some intermediates of biodegradation of several monoaromatic parent hydrocarbons under anoxic conditions. The hydrocarbons were detected downgradient of a crude oil spill in a shallow glacial outwash aquifer in Minnesota.

Table 2-4. Oxidized Intermediates of Several Volatile Monoaromatic Parent Hydrocarbons (after Cozzarelli et al., 1990).

PARENT	OXIDIZED INTERMEDIATE
Benzene	Phenol
Toluene	Benzoic Acid
o-xylene	o-toluic acid
m-xylene	m-toluic acid
p-xylene	p-toluic acid
1-ethyl-2-methylbenzene	Unknown
1-ethyl-3-methylbenzene	m-methylphenylacetic acid
1-ethyl-4-methylbenzene	p-methylphenylacetic acid
1,3,5-trimethylbenzene	3,5-dimethylbenzoic acid
1,2,4-trimethylbenzene	2,4-dimethylbenzoic acid, 2,5-dimethylbenzoic acid, 3,4-dimethylbenzoic acid
1,2,3,5-tetramethylbenzene	2,4,6-trimethylbenzoic acid, 2,3,5-trimethylbenzoic acid

Aerobic degradation studies on sulfolane and diisopropanolamine (DIPA) by Fedorak et al., (1997) identified two metabolites of DIPA; monoisopropanolamine and methyl glyoxal. These compounds also served as growth substrates for bacteria responsible for the parent compound's biodegradation. Sulfolane was also degraded under aerobic conditions but metabolites could not be identified.

2.3.7 OTHER FACTORS AFFECTING BIODEGRADATION

The presence of a microbiological population in the subsurface capable of biodegrading a contaminant does not ensure that bioremediation will occur (Lewandowski and DeFilippi, 1998). A site's environment and geochemistry must be favourable for microbiological growth and maintenance. Environmental factors such as pH, temperature, contaminant concentration, site geology and nutrient availability can determine whether or not biodegradation will occur. Subsurface variability is also recognized as a controlling factor by regulatory agencies. For example, the USEPA's National Center for Environmental Research and Quality Assurance (NCERQA, 1999) is currently conducting a series of studies to examine processes controlling anaerobic bioattenuation of dissolved hydrocarbons in groundwater. At each site studied, spatial variations in contaminant biodegradation rates, sediment characteristics, and microbiological populations will be examined.

While some microorganisms grow in pH conditions ranging from 4 to 10, most grow in pH conditions ranging from 6 to 8. Decreases in pH over the duration of the natural attenuation period can result in a decrease of microbiological activity. Godsy et al., (1992) demonstrated that decreases in pH can occur downgradient of contaminant sources due to incomplete anaerobic degradation of aromatic compounds, resulting in volatile fatty acid accumulation within a plume. Therefore, low pH may be both an indicator of the occurrence of biodegradation as well as an indicator that inhibition of the biodegradation processes may potentially occur. A decrease in pH may also lead to carbonate dissolution. The presence of carbonate may act to buffer acids produced by bacteria and maintain groundwater at pH conditions more favourable for microorganism activity.

Metcalf and Eddy (1991) indicate that rates of many microbiological reactions double for each 10°C rise in temperature. In contrast, colder temperatures often slow biodegradation rates leading to longer completion times for biodegradation processes. Work by Herrington et al., (1997) demonstrated that microorganisms can become acclimatized to colder temperatures resulting in biodegradation rates similar to those in warmer climates.

At high concentrations, many organic contaminants become toxic to microorganisms (Lewandowski and DeFilippi, 1998). At sites containing free phase liquids, bioremediation may not be relied upon as the primary means of natural attenuation of a contaminant plume. Where biodegradation is active at the fringes of the free phase liquid, bioavailability of a contaminant will be controlled by the rate at which it dissolves into groundwater. If a contaminant has adsorbed onto aquifer matrix materials, bioavailability will also be controlled by the rate of desorption. As a dissolved phase is used up by microorganisms, the local concentration gradient increases resulting in desorption of the contaminant.

Higher concentrations of contaminants require greater amounts of electron acceptors and nutrients that may be of limited supply at a site. Conversely, at low concentrations in the microgram to nanogram range (Lewandowski and DeFilippi, 1998), contaminants may not provide enough energy or carbon essential for cell growth and maintenance. Contaminant mixtures, such as metals and organics, present at a site can also create problems for the success of biodegradation. The metals may be toxic to microorganisms involved in degradation of the organics, thereby limiting their success.

Site hydrogeology can also limit the success of natural attenuation. Low hydraulic conductivity soils such as clay or fine textured till can limit migration of the contamination and the movement and availability of essential electron acceptors and nutrients. When combined with a high hydraulic gradient, high hydraulic conductivity soils such as sand or gravel may facilitate too rapid a migration of the plume. As a result, the natural attenuation processes can be overwhelmed. Plume migration is also controlled by the sorptive capacity of soils and rate of biodegradation. The effectiveness of natural attenuation is inversely proportional to the distance of migration of the plume (USGS, 1998). If groundwater flow velocity is much greater than the sorptive capacity and the biodegradation rate, a plume will be relatively large and natural attenuation may not prevent exposure of potential receptors to unacceptable levels of contamination. If groundwater flow velocity is small relative to sorptive capacity and biodegradation rate, a plume will be relatively small and natural attenuation may be successful at preventing receptor exposure to unacceptable levels of contamination. Consequently, it is very important to understand the geology and hydrogeology of a site as well as their potential affect on natural attenuation as a whole.

The success of computer models used to predict behavior of expected natural attenuation processes depends on accuracy of data obtained during initial site characterizations. One aspect of site characterization that is susceptible to error is hydrogeologic interpretation of data obtained from monitoring wells. Brittle clay-rich geologic materials can develop interconnected fractures around the borehole during drilling. Consequently, groundwater (and contaminants) can migrate around the well seals with relative ease (Trojan, 1988). This can lead to misinterpretation of groundwater flow directions and gradients, incorrect hydraulic conductivity values, and potential contaminant migration through an aquitard. Modeling cannot account for the leakage and resulting groundwater monitoring programs may not pick up this short-circuit in the contaminant's movement across a site.

Ammonia-nitrogen and ortho-phosphate are limiting nutrients required for microbiological growth and activity. Ammonia is the preferred nitrogen source and ortho-phosphate is the preferred phosphorous source for most soil bacteria. It is possible that biodegradation rates and activities could be limited by low levels of these nutrients even if all other growth needs such as electron acceptors or carbon sources are available. Depletion of these nutrients as compared to background groundwater concentrations can also be used as an indicator of biodegradation of contaminants.

Dissolved oxygen may or may not be a limiting factor at a site. In situations where dissolved oxygen levels are low, anaerobic processes may facilitate the biodegradation of contaminants. For example, BTEX compounds have been shown to be biodegraded both aerobically and anaerobically. However, in general, dissolved oxygen levels less than 0.5 mg/L suggests that anaerobic conditions may exist. Aerobic degradation usually takes place when dissolved oxygen levels are between 3 and 5 ppm. Dissolved oxygen content can be related to soil moisture content. Soil saturation greater than 80% can reduce availability of oxygen and therefore affect bacterial activity (CPPI, 1995).

In the case of iron (III) reduction processes, Quigley and Banwart (1999) have shown that bioavailability of iron (III) can affect biodegradation of organic pollutants. Poorly crystalline forms of iron (III) and the presence of chelators capable of forming iron (III) complexes greatly increase bioavailability of the iron, which in turn increases biodegradation of a contaminant.

Too much iron precipitation can also be detrimental to other, more favourable bioremediation processes. For example, Lammey and Noseworthy (1997) noted that precipitation of ferrous iron greatly reduced the size of the zone of denitrification within a contaminant plume. Because denitrification supplies more energy to microorganisms, it is a more efficient degradation process. Efforts were made to increase the size of a denitrification zone by addition of nitrate rich fertilizer in monitoring wells.

Natural or introduced changes to a site's hydrogeochemistry can also affect natural attenuation of metal precipitates. For example, when landfill leachate enters an aquifer, biodegradation of organic matter in leachate can create anaerobic conditions that can induce the formation of reduced sulphur and iron species. Heavy metals are often also present in leachate and, under reducing conditions, can be expected to react with sulphide to form insoluble metal sulphide precipitates. However, once organic matter is degraded and anaerobic conditions revert to aerobic, it is possible that formerly precipitated metals such as cadmium may be mobilized in an aquifer. Altmann and Bourg (1997) demonstrated that cadmium sulphide precipitates could be remobilized once a groundwater system made the transition from anaerobic to aerobic. The major controlling factor for cadmium remobilization in the groundwater system was pH. At a pH of less than 6, cadmium was easily remobilized.

The physical state of a metal pollutant can govern its effective removal from soil. For example, the extent of pollution would be less severe with metal powders or metal objects than with a liquid containing dissolved metal salts. One major problem with metal attenuation is that most removal mechanisms involved can be reversed. That is because they are influenced mainly by adjustments to soil and pore water pH. These adjustments can occur on a localized scale due to changes in site development or recontamination. For natural attenuation to be considered for metals, it is also necessary to demonstrate that concentrations will be decreased prior to reaching a point of compliance and that metals are irreversibly adsorbed or trapped. Problems can arise when fresh recharge is introduced into the contaminated zone. Recharge creates desorption of metals as the sorbed fraction tries to equilibrate with the recharge.

Generally, the longer metal-rich solutions stay in contact with aquifer matrix minerals, the larger the irreversibly sorbed fraction becomes (Brady et al., 1998). Thus, limiting recharge could enhance natural attenuation of metals.

Reductive dechlorination of chlorinated solvents is only effective where there is an adequate supply of electron donors. Its use is therefore limited to sites where these donors exist and where the supply is sufficient to ensure that they will not be depleted before remediation is complete.

Colloids are mineral fragments such as clays, organic macromolecules, microorganisms or biological debris usually between 10^{-6} and 10^{-9} metres in length. They can be removed from groundwater when they aggregate and settle or when they are trapped by physical or chemical bonds. However, until this happens they can travel hundreds of metres in an aquifer (Brady et al., 1998). Metals and organics can be adsorbed onto colloids and travel with them through the aquifer matrix. This can result in contaminant transport beyond what can be predicted by modeling or by monitor well analysis unless colloids are specifically part of the analytical suite.

2.4 MODELING

Modeling is conducted to provide an estimate of the fate and transport behavior of contaminants of concern. Modeling provides an estimate of the migration potential of contaminants and the length of time contaminants will persist so that potential effects on downgradient receptors can be assessed. This can be achieved by allowing the model to run until steady state conditions are met. The distance a plume migrates can be compared to the distance to receptors, and decisions made regarding whether natural attenuation is appropriate for site remediation and risk management. Models can also be used to develop a groundwater monitoring program for a site by evaluating plume shape and migration patterns in two and three dimensions. This information can then be used to assist in placement of wells not only in terms of their location around a plume but also vertically within expected flow regimes. Modeling accuracy depends on the thoroughness of site characterization and input of as much site-specific information as possible. This includes information on site geology, hydrogeology, and geochemistry as well as information on degradation rates determined by microcosm and degradation rate studies. Models are an analytical representation of what might be expected to occur at a site. Mathematical equations are used to simulate effects to contaminants during transport within an aquifer matrix. Problems can occur when sites have complex geologies or multiple sources. Therefore, modeling predictions must always be followed by continued groundwater monitoring to ensure that the site behaves as predicted.

There are several models available for evaluating the fate and transport of contaminants in the environment. Three models, Bioscreen (USEPA, 1996a), MT3D (USEPA, 1990), Bioplume II / III (Rifai et al., 1987), will be discussed. These models were chosen because they are relatively easy to use and are available at no cost to the user. Bioscreen was developed for the Air Force Center for Environmental Excellence Technology Transfer Division (www.afcee.brooks.af.mil/) and is available to the public domain through the USEPA. MT3D and Bioplume II (and its replacement Bioplume III) are two of the more commonly used models for contaminant fate and transport evaluation. They are also available in the public domain through the USEPA (www.epa.gov/epahome/data.html). Additional documentation on these modeling programs can be obtained from Wiedermeier et al., (1999).

Bioscreen (USEPA, 1996a) is based on the Domenico analytical solute transport model and can simulate advection, dispersion, adsorption, and biodegradation processes. Domenico and Robbins (1985) demonstrated that a relatively simple extended pulse model can closely approximate more rigorous solutions to the advection-dispersion equation for a finite constant source. Domenico (1987) modified this extended pulse model to include first order decay. The revised model assumed constant regional flow and three-dimensional dispersion in a homogenous, isotropic, infinite aquifer. Bioscreen simulates biodegradation in one of two ways. It either uses a first order decay rate constant or else background concentrations of electron acceptors are entered and an instantaneous reaction is simulated. The first order decay constant approach combines the biodegradation parameters. The instantaneous reaction approach uses principles of superposition, and contaminant mass at any time and location can be calculated by subtracting 1 mg/L of dissolved organic mass for each 1 mg/L of biodegradation capacity supplied by the available electron acceptors.

Bioscreen (USEPA, 1996a) is a two dimensional model that is sometimes used to represent a three dimensional problem. Depending on the type of contaminant, it may not accurately represent the source of the contamination. This can lead to errors in estimating distance from centerline to outer edge of the plume. Bioscreen also seems to be highly sensitive to values for dispersivity chosen for a model run. Dispersivity is defined as a medium-dependent hydrodynamic parameter characterizing solute dispersion of a contaminant plume in a porous medium (Xu and Eckstein, 1997). Information for a case study discussed below indicated that if high dispersivity values were used, distance the contaminant plume migrated was significantly reduced. Longitudinal values for dispersivity of half of the expected actual site values had to be used in order to provide modeling responses similar to those determined by site monitoring.

MT3D (USEPA, 1990) was developed for use with a block-centered finite difference flow model such as Modflow. It assumes that changes in a plume concentration do not measurably affect the flow field. This allows the user to construct and calibrate a flow model independently. MT3D simulates biodegradation under first order decay conditions only. Inputs for diffusion coefficients, retardation factors and dispersivities can be entered into the model. Model output is contaminant concentration distribution at various time intervals. MT3D can accommodate confined and unconfined aquifer conditions, mass flux boundaries and solute transport effects from external sources such as wells, recharge areas or evapotranspiration sites.

MT3D can also provide time step simulations of contaminant concentrations. A time step is determined by the model based on grid spacing, groundwater velocity and dispersivity parameters. Sites with low groundwater velocities may require a large time step in order to attain a reasonable solution. With smaller time steps, the model may not project the contaminant particle far enough into the future to move the contaminant beyond the starting cell. This leads to the perception that the contaminant is not migrating. Bioplume II is a two-dimensional finite difference model for simulating biodegradation of hydrocarbons in groundwater under the influence of oxygen-limiting conditions (Rifai et al., 1987). The model computes changes in concentration over time due to advection, dispersion, mixing and biodegradation. The model does not consider dynamics of microbiological activity required to consume hydrocarbons and assumes that oxygen is the only electron acceptor used by microorganisms during biodegradation (Zhong et al., 1995). Bioplume III simulates both aerobic and anaerobic biodegradation processes in addition to advection, dispersion, adsorption, and ion exchange. The model simulates biodegradation of organic contaminants using a number of aerobic and anaerobic electron acceptors including oxygen, nitrate, iron (III), sulphate, and carbon dioxide. Simulations assume homogeneous conditions, steady state groundwater flow, a constant initial background dissolved oxygen concentration, and dissolved oxygen recharge upgradient of the source. The model tracks two plumes: oxygen and hydrocarbon. The two plumes are superimposed to determine resulting concentrations of oxygen (or other electron acceptors) and hydrocarbon at each time step. Three different kinetic expressions can be used to simulate aerobic and anaerobic biodegradation reactions. These include first order decay, instantaneous reaction and Monod kinetics. The major differences between Bioplume II and Bioplume III are that Bioplume III runs on a Windows environment instead of Bioplume II's DOS environment, that Bioplume III incorporates anaerobic processes, and that Bioplume II has been integrated with an environmental information system adopted by the U.S. Air Force (Rifai et al., 1987). The USEPA has issued a warning regarding the use of Bioplume III (www.epa.gov/epahome/data.html/). Apparently there is a problem with the first order decay option for the electron acceptors. To date, this problem has not been corrected.

3.0 EXISTING LEGISLATION

3.1 APPROACH TO OBTAINING LEGISLATIVE INFORMATION FROM OTHER JURISDICTIONS

In developing policy, guidelines, codes of practice, or regulations for natural attenuation, it is useful to examine legislation already in existence in other regulatory agencies. Contact and discussion with these agencies allow for a better understanding of the motivation for developing the policy, how the policy was developed, what the policy content is, what input from the public and other stakeholders was allowed or considered when forming the policy, how the policy is administered and implemented, and problems or benefits associated with that policy. It also allows for an examination of a policy and a determination as to whether it can be adopted as is, with minor changes or additions, or whether a policy specific to the reviewing agency is required. The benefits of not "re-inventing the wheel" are that a researched, useable, functional, and workable policy can be put in place quickly and that administrators of the adopted policy can be trained quickly.

Regulatory agencies have published numerous documents related to natural attenuation. Review of all these documents was beyond the need or scope of the research into existing legislation. Though some insight can be gained as to the process of the review of natural attenuation by regulators and its eventual acceptance, the fact is that natural attenuation is documented as a viable remediation alternative. Therefore, a documentation of the history of natural attenuation was not deemed necessary for the objective of reviewing existing legislation. However, in many instances, these older documents were consulted for insight into issues such as public consultation and the need for, and requirements of, adequate site characterization to support the use of natural attenuation.

Currently, there are no regulatory agencies in Canada which have a formal policy specific to natural attenuation as a remediation/site management option. The Federal Government is working in co-operation with its armed forces in examining the use of natural attenuation and will inevitably be required to develop a policy.

The Environment Departments of both British Columbia and Ontario were contacted by e-mail and telephone to determine whether natural attenuation is an acceptable remediation alternative and, if so, how applications for its use are considered. Both provinces do not directly mention natural attenuation but refer to natural processes to different degrees (BC, 1999; MOEE, 1996). Alberta has begun the process of including natural attenuation when considering the remediation of upstream oil and gas lease sites and risk assessment and management options (AENV, 1999a and b). A more detailed discussion of each province's legislation follows below.

The United States Environmental Protection Agency (USEPA) has issued several documents regarding natural attenuation. A complete listing of those publications can be found in the USEPA publications website (www.epa.gov/cinc/). The main documents reviewed for technical requirements and protocols for site investigations to support the implementation of natural attenuation were *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*, April 1999 (USEPA, 1999) and *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*, 1998 (USEPA, 1998).

The United States Department of Defense (DOD) has also developed policy and protocols for the investigation and use of natural attenuation at its military bases (Wiedermeier et al., 1995). The preface to those documents also indicates that persons outside the military can also use the protocol. The documents can be obtained as a toolkit for use by interested parties by contacting the Air Force Center for Environmental Excellence on their website (www.afcee.brooks.af.mil/). The main document, *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater*, (Wiedermeier et al., 1995) was developed for the DOD by the United States Air Force Center for Environmental Excellence in San Antonio, Texas.

The American Society for Testing and Materials (ASTM) has also a document related to natural attenuation and bioremediation (ASTM, 1998). A complete listing for their documents can be found by searching their website (www.astm.org/). The main document *Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites*, 1998 (ASTM, 1998), was reviewed for information regarding technical requirements in support of the use of natural attenuation.

As part of this study, individual states in the United States were contacted regarding formal policy development. First, all 50 states were evaluated for formal policy regarding natural attenuation via searches conducted on the internet. Environmental department documents for each of the states were searched. Relevant documents were downloaded for later review from each of the state's having a formal natural attenuation policy. If no documents were found the environment departments were contacted via e-mail for information regarding policy, regulations or guidelines pertaining to natural attenuation. The departments were asked if they had a formal policy on natural attenuation and whom to contact for more information. A formal policy is defined here as documents or legislation specifically written for natural attenuation. Acceptance of natural attenuation by a regulator on a case-by-case basis under general site remediation guidelines or regulation was not seen as formal policy. However, lack of a formal policy does not mean that natural attenuation is not considered. The purpose of the preliminary screening was to categorize the states as to whether they did or did not have a formal policy on the use of natural attenuation and whether they had developed their own policy. Contacts for states with formal polices were sent an evaluation questionnaire as a starting point for information collection and as a means of selecting representative states for review as discussed below. A copy of the questionnaire is included in Appendix A. Information obtained from the questionnaire was useful in clarifying issues related to limitations placed on MNA use by a regulator or the role of public participation. However, the questionnaire did not provide significant additional information on the content of a particular policy, regulation, or guideline. Additional information on natural attenuation was sought by telephoning the environment department contact who responded to the questionnaire. This step was included to clarify understanding of the legislation, discuss the state's approach to implementation of natural attenuation, and discuss case studies where natural attenuation had been implemented.

Documents selected for review from the website searches were reviewed for relevant sections on natural attenuation, site investigation, site closure, and remediation objectives. Information from these sections were included in the discussion of each state's legislation. This discussion was first written while waiting for responses to questionnaires and then revised based on response to the questionnaires and discussion with the state contact person.

There are some inherent problems associated with the approach taken to complete the research. This may have led to states with formal policies being overlooked. Contact via e-mail relies upon the internet representative having a firm grasp of all the business of the environment department. If the representative is unaware that a certain division or group within an environment department deals with natural attenuation this may result in a response that the particular state does not have a formal policy on that subject. The writer also has no knowledge of either the structure of the environment department or the responsibilities of the different groups within that department. Therefore, it is possible that the wrong government department may have been contacted for information. It is also possible that natural attenuation could be dealt with by two different divisions within an environment department, requiring two different contacts to be made. Such was the case with the State of Utah where issues related to underground storage tanks and issues related to other wastes are dealt with by two different divisions. Policies related to natural attenuation are not always referred to by that name. For example, until recently, the State of Florida dealt with natural attenuation under "monitoring only plans" rather than formally calling it natural attenuation (FDEP, 1998). Therefore, questionnaires sent to the various environment department contacts as part of the research were carefully worded to ensure that policies were not overlooked due to differences in terminology.

Of 50 states contacted, 26 had an informal policy on natural attenuation. An informal policy means that contaminated sites are be dealt with on a case-by-case basis and either the USEPA (1998, 1999) or DOD (Wiedermeier et al., 1995) documents would form the basis of a review of an application to the regulator by a proponent to use natural attenuation at a site. Table 3-1 shows a generalized breakdown of U.S. state

Table 3-1. Generalized Breakdown of U.S. State Natural Attenuation (NA) Policies.

States with Informal Policy or Guidelines on NA		States Using Existing USEPA or ASTM Protocols for NA Review	States not Accepting Natural Attenuation	States With Formal NA Policy	Contaminants Governed by Formal NA Policy
California	Iowa	Pennsylvania	Arizona	Michigan	Petroleum Hydrocarbons, Other Contaminants
Arkansas	Kansas	Washington		Wisconsin	Petroleum Hydrocarbons, Other Contaminants
Maryland	Vermont	Maine		Florida	Petroleum Hydrocarbons
Wyoming	Tennessee	Colorado		Utah	Petroleum Hydrocarbons
Rhode Island	Ohio	Alabama		Minnesota	Petroleum Hydrocarbons, Other Contaminants
Hawaii	Idaho	Oregon		North Carolina	Petroleum Hydrocarbons, Other Contaminants
New York	Indiana	Delaware		South Carolina	Petroleum Hydrocarbons
West Virginia	New Jersey	Mississippi		Texas	Petroleum Hydrocarbons, Other Contaminants
Connecticut	Massachusetts	Montana		New Hampshire	Petroleum Hydrocarbons, Other Contaminants
North Dakota	Kentucky	New Mexico		Alaska	Petroleum Hydrocarbons, Other Contaminants
South Dakota	Virginia	Nebraska			
Nevada	Illinois	Louisiana			
Georgia	Oklahoma				
Missouri					

natural attenuation policies. For states with a formal policy, contaminants governed by that policy are also listed.

Originally states were to be grouped by a more formal categorization method outlined in Table 3-2 in order to reduce the anticipated size of the task of reviewing each the states with a formal natural attenuation policy. All states with a formal policy on natural attenuation were to be included in this step. However, once research revealed that very few states had a formal natural attenuation policy, this categorization step was eliminated.

Table 3-2. Proposed Selection Criteria for Grouping of States with a Formal Natural Attenuation Policy.

Category	Descriptor	Descriptor
Population Size	Large	Small
Winter Climate	Cold Winters	Warm Winters
Surficial Geology	Thick clayey/silty soils	Thin soils or sandy/gravelly soils
Geographic Location	Inland	Coastal
USEPA Region	One from each Region (if possible)	
Groundwater Usage	High	Low

A total of eight of the ten states with a formal policy were reviewed (Table 3-1). These states were selected to provide a representative view of the existing legislation and practices adopted by those states and allow for their methods to be reviewed in the context of Alberta specific conditions. South Carolina and North Carolina were not reviewed in detail as their respective legislation did not vary significantly from the eight states that were reviewed. States were chosen from a range of potential climates and soil conditions to examine what effect these differences might play in the application of the regulations. Other goals in selecting these states were to determine the motivation of a state for developing its own policy, the procedure used for developing that policy and subsequent regulations or guidelines, the consultative approach, (both internal and external) used to review the policy, the approach to implementing the policy, and to gain feedback from regulators and industry regarding the implementation of a policy at contaminated sites. The following states were selected: Alaska, Florida, Michigan, Minnesota, Utah, New Hampshire, Texas, and Wisconsin.

3.2 REVIEW OF EXISTING LEGISLATION

3.2.1 CANADA

3.2.1.1 Federal

The Canadian Federal government does not have a formal policy on the use of natural attenuation. Its use is considered on a site-by-site basis. Existing USEPA and DOD protocols (USEPA, 1998, 1999 and Wiedermeier et al., 1995) are used in the evaluation of data submitted by a proponent.

3.2.1.2 Ontario

The Ontario Water Resources Act (1990) charges the Ontario Ministry of Environment and Energy (MOEE) with conservation of groundwater resources in the Province of Ontario. Discharges of contaminants into groundwater are divided into two categories each with their own guidance. Discharges at sites are dealt with under Guide B-7, *Incorporation of the Reasonable Use Concept into MOEE Groundwater Management Activities*, April 1994 (MOEE, 1994a). Discharges at sites not requiring an approval or discharges from spills are dealt with under Guide B-9, *Resolution of Groundwater Quality Interference Problems*, April, 1994 (MOEE, 1994b).

Guide B-7 establishes the reasonable use of groundwater on properties adjacent to sources of contamination and determines the limits on discharge of contaminants from facilities approved by MOEE that are used for disposal of waste into shallow groundwater (MOEE, 1994a). The concept of reasonable use was introduced due to recognition of variability in quality, quantity and availability of groundwater in Ontario.

The Regional Director has the responsibility for establishing reasonable use based on input from the facility owner, MOEE staff and, in the case of major issues, the public.

Reasonable current and potential uses are established using three main considerations:

- Present use of groundwater in vicinity of the contamination
- Potential use of groundwater in vicinity of the contamination
- Existing quality and quantity of groundwater in vicinity of the contamination

Potential use of the groundwater is almost always thought to be for domestic supplies due to the availability and quality of groundwater across the province. Adjacent land uses such as agricultural activities and utility corridors can also affect the reasonable use designation.

The MOEE also specifies locations where potential placement of waste disposal facilities may not be appropriate. These include:

- Areas where no appreciable attenuation can be provided
- Areas where natural attenuation capacity is weak
- Areas where the subsurface is suited to a better use
- Areas where consequences of failure are unacceptable

Determination of contamination limits and definition of an attenuation zone are dealt with in Procedure B-7-1 (MOEE, 1996). In this guide, the purpose of a contaminant attenuation zone is to allow limited impairment of off-site property by means of easements or other methods without imposing severe restrictions on land use listed above which apply to a waste disposal site (MOEE, 1996). The attenuation zone lies outside a waste disposal site and is delineated both with respect to area of land that it underlies and with respect to its depth. Within the zone, it is intended that contaminants will be attenuated to levels compatible with reasonable use of the adjacent properties as defined in Guide B-7 (MOEE, 1994a). An agreement between the facility owner and the adjacent landowner as to use of the zone must be reached and should be registered on the land title.

The MOEE may support an application for attenuation in the following circumstances:

- Where an alternate water supply that is superior to any associated with the attenuation zone is available
- Where a contaminant zone is limited and clearly defined
- Where high levels of dissolved solids (iron, manganese, or total dissolved solids) are present in groundwater associated with the attenuation zone
- Where the Regional Director judges appropriate use to be an attenuation zone regardless of its suitability for other purposes

Guide B-7 (MOEE, 1994a) recommends that future use of attenuation zone property be strictly controlled. These controls should be permanent or until such time as it can be proven that they are no longer needed.

Guide B-9 (MOEE, 1994b) deals with impacts to the quality of groundwater supplies due to discharges at closed facilities or discharges resulting from spills. This guide governs discharges following pathways from surface to the subsurface, from subsurface to the surface and pathways within the subsurface. The facility owner is responsible for all costs associated with site investigation, remediation of the environment and restoration of affected water supplies. The level of remediation is determined on a case-by-case basis but no mention is made of the concept of reasonable use in the Guide. The adjacent landowner can also initiate restoration and recover costs from the facility owner. The facility owner must submit an action plan to MOEE establishing a method of remediation and a time frame for remediation.

3.2.1.3 British Columbia

British Columbia's (BC) Municipal Waste Reduction Branch has prepared *Guidelines for Environmental Monitoring at Municipal Solid Waste Landfills*, January, 1996 (BC, 1996). The guidelines provide a definition for attenuation and mention remedial action should the analytical data indicate an upward trend in concentration or results above the applicable regulatory criteria. However, natural attenuation is not dealt with as a specific remediation option. The *Regulation of Petroleum Hydrocarbons in Water under the Contaminated Sites and Special Waste Regulation* (BC, 1999) specifies that certain criteria must be met in surface and ground waters "at the downgradient property boundary of the petroleum hydrocarbon contaminated site, or on any property of any other site(s) that may be affected by migration of petroleum hydrocarbon contamination" and that remediation must occur if the criteria are exceeded. However, natural attenuation is not discussed as a means of preventing the migration of the contamination to the property boundary.

When determining what criteria to use at a site, facility owners have three options. They may choose to remediate to existing default criteria, they may choose criteria based on a generic risk assessment, or they may choose to modify the generic risk assessment model by incorporating site specific information and generating site specific criteria. The current mathematical model used by the BC Ministry of Environment models hydrocarbon transport from soil into groundwater and then ultimately to an aquatic receptor. The model can use a water well as an ultimate receptor. Petroleum hydrocarbons are the only contaminants considered by the model. The model assumes a set pathway length and that no biodegradation occurs within the aquifer. However, proponents can modify pathway length and add in biodegradation or other attenuation type parameters, provided these changes are supported by data from the site. Details for evaluating biodegradation or other attenuation factors are not discussed. Greater detail for deriving site-specific criteria can be found in the Ministry document *Methods for Deriving Site-Specific Water Quality Objectives in British Columbia and Yukon* dated November, 1997.

3.2.1.4 Alberta

Alberta Environment (AENV) has developed two documents which contain a reference to natural attenuation. Those documents are:

- *A Proposed Management Framework and Associated Remediation Objectives for Upstream Oil and Gas Sites in Alberta* (AENV, 1999a)
- *Policy for Management of Risks at Contaminated Sites in Alberta* (AENV, 1999b)

The purpose of the management framework document (AENV, 1999a) is to outline a proposed administrative and technical framework for managing contamination at only upstream oil and gas sites such as wellheads or compressor stations. The document defines unconditional, conditional and deferred states of closure for upstream sites using risk-based criteria. Unconditional closure sites are those that do not require additional remediation. Conditional closure and deferred closure sites are those where ongoing remediation is required to meet remediation objectives. At those sites, natural attenuation can be used when developing site closure strategies. Draft guidelines for Phase I and Phase II site assessments for oil and gas lease sites are currently under development (Nason, 1999). The guides will require a facility owner to provide preliminary support for the use of natural attenuation at a site.

The policy for risk management (AENV, 1999b) provides general guidance for establishing or modifying risk-based remediation objectives and applying site-specific risk assessment and management to meet AENV objectives. The concept of risk management is divided into two categories: remediation and exposure prevention. The remediation category includes physical, chemical and biological treatment to reduce contamination to acceptable levels appropriate for a particular land use category. Natural attenuation could be considered under the remediation category. However, no details regarding the characterization or evaluation of natural attenuation are provided.

The risk management guidelines do not allow for impairment of offsite property above applicable land use objectives without that adjacent landowner's consent. If the facility owner cannot obtain consent, AENV may require specific objectives to be met at the property line. Remediation of the adjacent affected property must also meet those objectives.

3.2.2 UNITED STATES

3.2.2.1 United States Environmental Protection Agency

The two main documents reviewed were *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*, April 1999 (USEPA, 1999) and *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* 1998 (USEPA, 1998).

A. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites (USEPA, 1999).

The purpose of this Directive is to clarify USEPA's policy regarding use of monitored natural attenuation (MNA) for cleanup of contaminated soil and groundwater in the Superfund, RCRA Corrective Action, and Underground Storage Tank programs. It provides a rationale for implementation of the policy and a discussion of background to natural attenuation processes. This background discusses specific issues related to contaminants of concern, transformation products, and cross-media transfer.

The Directive advocates a three-tiered approach to determining and demonstrating the efficacy of MNA as a remediation option. The tiered approach requires three lines of evidence to be provided as evidence of natural attenuation at a site.

These lines of evidence are (USEPA, 1999):

- Historical groundwater and/or soil analytical data to demonstrate a clear and meaningful trend of decreasing contaminant mass and /or concentration over time at appropriate monitoring or sampling points. Migration of contaminants should not be the sole reason for the reduction seen.
- Hydrogeologic and chemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes active at a site, and the rate at which processes will reduce contaminant concentrations to required levels.
- Data from field or microcosm studies which directly demonstrate the occurrence of a particular natural attenuation process at a site and its ability to degrade contaminants of concern.

The first line of evidence of information may be acceptable to prove natural attenuation if the data provided are deemed of sufficient quality and duration. Usually this is not the case and the second line of evidence is required for a site. Data from microcosm studies are only deemed necessary where information for the first two lines of evidence is seen as inadequate.

The Directive includes guidance as to sites where MNA may be appropriate. The Directive states that "USEPA expects that MNA will be most appropriate when used in conjunction with other remediation measures (e.g., source control, groundwater extraction), or as a follow-up to active remediation measures that have already been implemented" (USEPA, 1999). Several factors for consideration of MNA at a site are presented including:

- Whether contaminants at a site are likely to be remediated by natural attenuation processes
- Stability of a groundwater plume and potential for further migration
- Potential for unacceptable risks to receptors, both environmental and human.

Source control is seen as an important part of the remediation approach to any site where MNA is being considered.

The Directive also discusses the concept of reasonable time for site remediation. The idea is that MNA must be able to attain remediation objectives for a site in a timeframe comparable to that of other appropriate remedial alternatives. Items to be considered when evaluating reasonable timeframes include:

- Classification of the affected resource and potential requirement for future use
- Plume stability
- Uncertainties regarding contaminant mass and predictive capability of the site conceptual model
- Reliability of institutional controls and long-term monitoring
- Public acceptance of the predicted timeframe
- Ability of the proponent to fund required monitoring or contingency remedies over the predicted remediation timeframe

The timeframe required for MNA is recognized to likely be longer than that for other more active approaches to site remediation. Therefore, proper performance monitoring and contingency remedies are seen as the key to dealing with uncertainties in the above items.

Performance monitoring and evaluation are also seen as a critical aspect of any proposal for MNA. The Directive recommends that the monitoring program should be designed to accomplish the following items:

- Demonstrate that natural attenuation is occurring according to expectations
- Detect changes in environmental conditions with time or site development that may reduce effectiveness of natural attenuation processes
- Identify any potentially toxic and/or mobile transformation products
- Verify that a plume is not expanding

- Verify that no unacceptable effects to downgradient or onsite receptors are occurring
- Detect new releases to the environment that could adversely affect effectiveness of natural attenuation
- Verify that remediation objectives are being met

The Directive further recommends that monitoring continue after objectives have been met to ensure that there is no threat to human health or to the environment.

Contingency remedies must be included with the proposal for implementation of MNA. There must be flexibility in contingency measures to accommodate changes in site conditions or information, and risk or the development of new remediation technologies. The Directive recommends that trigger criteria be established prior to implementation of a remediation program that will indicate when contingency measures must be implemented. These criteria could include increasing trends in contaminant concentration, unexpected expansion of a contaminant plume to previously unaffected monitoring wells, evidence from monitoring that MNA alone will not meet the remediation objectives, and changes to land use or groundwater use that compromise the protectiveness of MNA.

B. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water (USEPA, 1998).

The purpose of this Protocol is to present a technical protocol for data collection and analysis to evaluate monitored natural attenuation through biological processes for remediating groundwater contaminated with mixtures of fuels and chlorinated aliphatic hydrocarbons (USEPA, 1998). The Protocol is aimed at improving the characterization process for sites where natural attenuation is being considered as a remediation option. Table 3-3, adapted from the Protocol, lists contaminants covered under it. This Protocol focuses on technical details needed to evaluate natural attenuation as a remediation option rather than on policy issues. In addition, the Protocol provides a flow chart for evaluation

Table 3-3. Contaminants Considered in the USEPA Technical Protocol for Chlorinated Solvents (after USEPA, 1998)

Abbreviation	Chemical Abstracts Service (CAS) Name	CAS Number	Other Names	Molecular Formula
PCE	Tetrachloroethene	127-18-4	Perchloroethylene, Tetrachloroethylene	C_2CL_4
TCE	Trichloroethene	79-01-6	Trichloroethylene	C_2HCl_3
1,1-DCE	1,1-Dichloroethene	75-35-4	1,1-Dichloroethylene, Vinylidine Chloride	$C_2H_2Cl_2$
trans-1,2,-DCE	(E)-1,2-Dichloroethene	156-60-5	trans-1,2-Dichloroethene, trans-1,2-Dichloroethylene	$C_2H_2Cl_2$
cis-1,2-DCE		156-59-2	cis-1,2-Dichloroethene, cis-1,2-Dichloroethylene	$C_2H_2Cl_2$
VC	Chloroethene	75-01-4	Vinyl Chloride, Chloroethylene	C_2H_3Cl
1,1,1-TCA	1,1,1-Trichloroethane	71-55-6		$C_2H_3Cl_3$
1,1,2-TCA	1,1,2-Trichloroethane	79-00-5		$C_2H_3Cl_3$
1,1-DCA	1,1-Dichloroethane	75-34-3		$C_2H_4Cl_2$
1,2-DCA	1,2-Dichloroethane	107-06-02		$C_2H_4Cl_2$
CA	Chloroethane	75-00-3		C_2H_5Cl
CF	Trichloromethane	67-66-3	Chloroform	$CHCl_3$
CT	Tetrachloromethane	56-23-5	Carbon Tetrachloride	CCl_4
Methylene Chloride	Dichloromethane	75-09-2	Methylene Dichloride	CH_2Cl_2
CB	Chlorobenzene	108-90-7		C_6H_5Cl
1,2-DCB	1,2-Dichlorobenzene	95-50-1	o-Dichlorobenzene	$C_6H_4Cl_2$
1,3-DCB	1,3-Dichlorobenzene	541-73-1	m-Dichlorobenzene	$C_6H_4Cl_2$
1,4-DCB	1,4-Dichlorobenzene	106-46-7	p-Dichlorobenzene	$C_6H_4Cl_2$
1,2,3-TCB	1,2,3-Trichlorobenzene	87-61-6		$C_6H_3Cl_3$
1,2,4-TCB	1,2,4-Trichlorobenzene	120-82-1		$C_6H_3Cl_3$
1,3,5-TCB	1,3,5-Trichlorobenzene	108-70-3		$C_6H_3Cl_3$
1,2,3,5-TECB	1,2,3,5-Tetrachlorobenzene	634-90-2	1,2,3,5-TCB	$C_6H_2Cl_4$
1,2,4,5-TECB	1,2,4,5-Tetrachlorobenzene	95-94-3		$C_6H_2Cl_4$
HCB	Hexachlorobenzene	118-74-1		C_6Cl_6
EDB	1,2-Dibromomethane	106-93-4	Ethylene Dibromide, Dibromomethane	$C_2H_4Br_2$

of information gathered to support the use of natural attenuation at a site. The flow chart guides the proponent through an initial screening process in which preliminary site data are used to determine the potential for natural attenuation at a site. If the screening process indicates there is potential for natural attenuation addition data are collected.

Section 2 of the Protocol provides detail not only on the types of information required for the initial screening process and subsequent investigation phases but also some guidance as to how to collect the information. Section 2 also provides a discussion of the initial site screening process. The screening process, undertaken once initial chemical and geochemical analysis have been conducted, involves the following steps:

- Determining if geochemical data indicate that biodegradation is occurring. If data are not sufficient, additional analysis is necessary
- Determining groundwater flow and solute transport parameters from field data (site characterization)
- Locating sources and potential points of exposure
- Estimating the biodegradation rate constant
- Comparing the rate of transport to the rate of biodegradation. This can involve modeling
- Determining if the screening criteria are met

The first step of the screening process is a scoring procedure that grades the amount of initial information available for a site in relation to its support for biodegradation. The scoring procedure is used by the regulator to evaluate the potential for natural attenuation at a site. Points are given for contaminant and geochemical analytical data based on whether they support the possibility of biodegradation occurring (e.g., presence of parent and daughter compounds, electron acceptors, etc.) and whether data fall within appropriate ranges for each parameter for biodegradation to potentially occur at a site. Table 3-4 lists parameters considered by the Protocol and their associated score based on data interpretation for each parameter as per Table 3-4. Points for data are then totaled. A total score of 0 to 5 points indicates inadequate evidence for anaerobic biodegradation.

Table 3-4. USEPA Chlorinated Solvents Screening Process Analytical Parameters, Interpretation, and Associated Score (after USEPA, 1998)

Analysis	Concentration in Zone of Highest Contamination	Interpretation	Score
Oxygen[a]	<0.5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations	3
Oxygen[a]	>5 mg/L	Not tolerated; however, VC may be oxidized aerobically	-3
Nitrate[a]	<1 mg/L	At higher concentrations may compete with reductive pathway	2
Iron (II)[a]	>1 mg/L	Reductive pathway possible	3
Sulphate[a]	<20 mg/L	At higher concentrations may compete with reductive pathway	2
Sulfide[a]	>1 mg/L	Reductive pathway possible	3
Methane[a]	<0.5 mg/L >0.5 mg/L	VC oxidizes Ultimate reductive daughter product, VC accumulates	0 3
Redox Potential[a]	<50 millivolts <-100 mV	Reductive pathway possible Reductive pathway likely	1 2
pH[a]	5<pH<9 5>ph>9	Optimal range for reductive pathway Outside optimal range	0 -2
TOC	>20 mg/L	Carbon and energy source, drives dechlorination	2
Temperature[a]	>20 °C	Promotes accelerated biochemical processes	1
CO_2	>2x Background	Ultimate oxidative daughter product	1
Alkalinity	>2x Background	Results form interaction of CO_2 and aquifer minerals	1
Chloride[a]	>2x Background	Daughter product of organic chlorine	2
Hydrogen	>1 nM	Reductive pathway possible, VC may accumulate	3
Hydrogen	<1 nM	VC oxidized	0
Volatile Fatty Acids	>0.1 mg/L	Intermediates resulting from biodegradation of more complex compounds; carbon and energy source	2
BTEX[a]	>0.1 mg/L	Carbon and energy source; drives dechlorination	2
PCE		Material released	0
TCE[a]		Material released Daughter product of PCE	0 2[b]
DCE[a]		Material released Daughter product of TCE	0 2[b]
VC[a]		Material Released Daughter product of DCE	0 2[b]
1.1.1-TCA[a]		Material released	0
DCA		Daughter product of TCA under reducing conditions	2
CCl_4		Material released	0
Chloroethane[a]		Daughter product of DCA or VC under reducing conditions	2
Ethene/Ethane	>0.01 mg/L >0.1 mg/L	Daughter product of VC or Ethene	2 3
Chloroform		Material released Daughter product of Carbon Tetrachloride	0 2
Dichloro-methane		Material released Daughter product of chloroform	0 2

[a] Analysis required in protocol [b] points only awarded for daughter product evidence

A score of 6 to 14 points indicates limited evidence, a score of 15 to 20 points adequate potential and a score of >20 points strong evidence for anaerobic biodegradation. A score of 15 or more indicates that the proponent can proceed to step 2 of the screening process which is site characterization. A more detailed description of the scoring system is provided in the Protocol.

Appendix A of the Protocol provides details regarding field investigation methodologies for a detailed site characterization. Information is provided on sampling techniques, investigation methods and quality assurance for sample collection. Appendix B provides a discussion on important processes affecting fate and transport of organic compounds in the subsurface. A description of each mechanism, such as advection or dispersion, is provided and equations given to assist with evaluation of those processes at the subject site. Appendix C provides detail on the interpretation of data and the calculations necessary to evaluate and document natural attenuation at a site. This appendix addresses tasks that must be completed to document natural attenuation including evaluation and presentation of site characterization and analytical data. Details are also provided as to how to design, implement and interpret microcosm studies.

3.2.2.2 United States Department Of Defense

On November 11, 1995, The Air Force Center for Environmental Excellence issued *Technical Protocol for Implementing Intrinsic Remediation with Long –Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (Wiedermeier et al., 1995). In this document, intrinsic remediation is defined as a remedial approach that relies on natural attenuation to remediate contaminants in the subsurface.

The purpose of this document is to provide a technical protocol for the collection and analysis of data used to support natural attenuation with long-term monitoring at U.S. Air Force sites. The document is intended for use by Air Force personnel and their consultants but has been used by other scientists, consultants, and regulatory personnel. The document deals specifically with fuel hydrocarbons. It describes processes involved in natural attenuation, site characterization activities carried out to support the use of natural attenuation, information regarding models to determine fate and transport of contaminants, and post implementation activities used to verify effectiveness of natural attenuation at a site.

The document suggests that three lines of evidence must be satisfied for a proponent to prove that human health and the environment are protected under a remediation scheme involving natural attenuation. These lines of evidence are (Wiedermeier et al., 1995):

- Documented loss of contaminants at the field scale
- Contaminant and geochemical analytical data
- Direct microbiological evidence

The first line of evidence involves historical trends in contaminant concentration together with relevant hydrogeological information to support that a loss of contaminant mass is occurring at the site. The second line of evidence involves quantitative evaluation of analytical data in mass balance equations to show that decreases in contaminant and electron acceptor concentrations can be directly correlated to increases in metabolic by-product concentrations (Wiedermeier et al., 1995). The third line of evidence involves determining that biota from a site are capable of degrading contaminants of concern. This approach to gathering evidence in support of natural attenuation is termed a "weight-of-evidence" approach in the document.

Data collected during site characterization can be used to simulate fate and transport of contaminants using modeling. The purpose of modeling is to allow for prediction of future behavior, extent and concentration of a dissolved plume. Modeling has three objectives:

- Predict the future extent and concentrations of a dissolved contaminant plume by simulating the combined effects of advection, dispersion, sorption and biodegradation

- Assess the potential for downgradient receptors to be exposed to contaminant concentrations that exceed regulatory levels intended to be protective of human health and the environment
- Provide technical support for an intrinsic remediation option at post-monitoring regulatory negotiations (Wiedermeier et al., 1995).

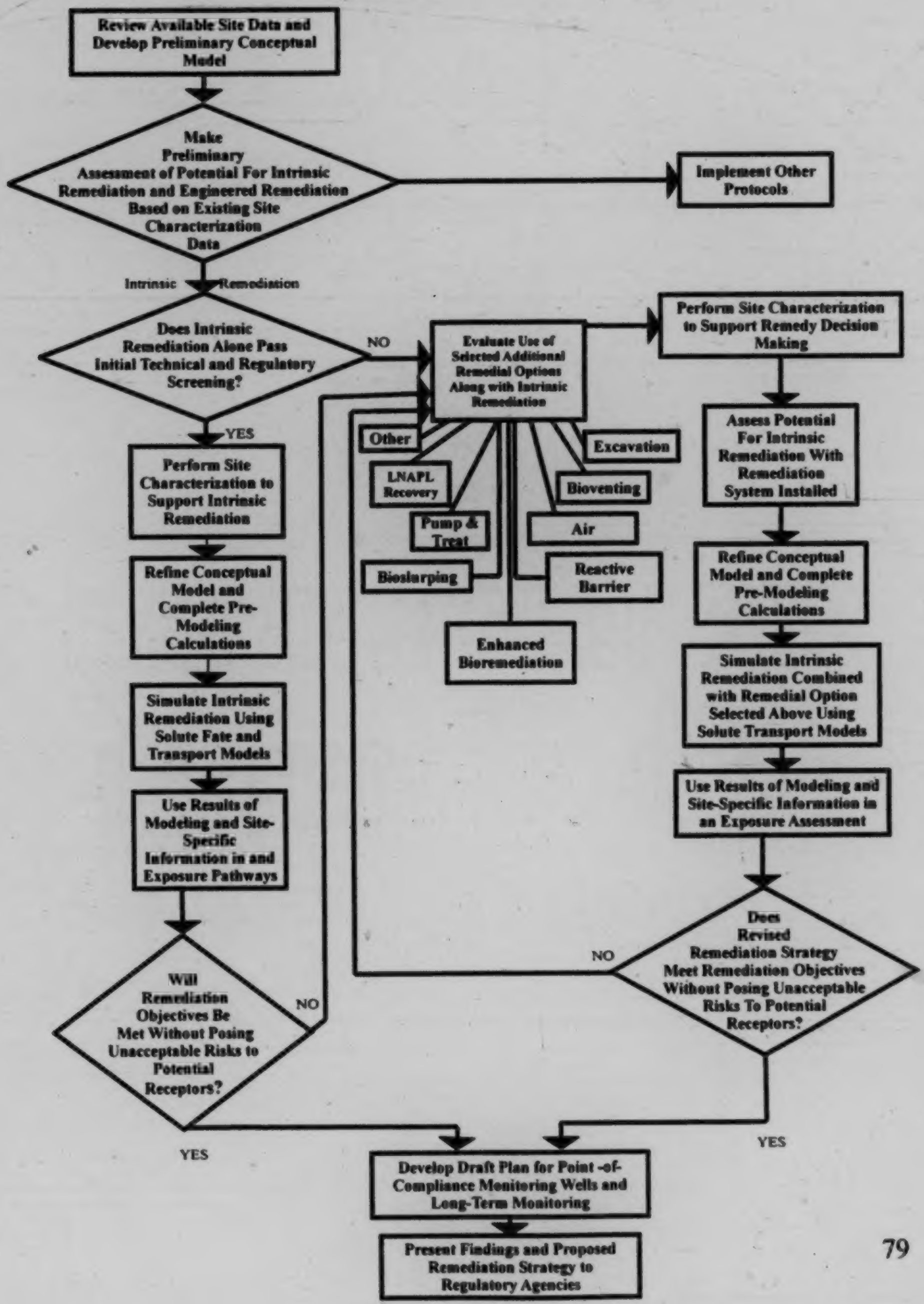
Modeling predictions can also be used for exposure pathway predictions. If natural attenuation will mitigate all suspected pathways, as demonstrated by modeling, its use at a site is further supported.

Wiedermeier et al., (1995) provides a protocol for implementing intrinsic remediation. This protocol describes the sequence of steps that should be followed to gather data necessary for modeling a plume and ultimately to support implementing natural attenuation. The steps include:

- Review available site data
- Develop preliminary conceptual model and assess potential for intrinsic remediation
- If potentially appropriate, perform site characterization in support of intrinsic remediation
- Refine conceptual model based on site characterization data, complete pre-modeling calculations, and document indicators of intrinsic remediation
- Simulate intrinsic remediation using analytical or numerical solute fate and transport models that allow incorporation of biodegradation term, as necessary
- Conduct an exposure pathway analysis
- If intrinsic remediation alone is acceptable, prepare long-term monitoring plan
- Present findings to regulatory agencies and obtain approval for intrinsic remediation with long-term monitoring option

These steps and the decisions associated with each are summarized in Figure 3-1, adapted from Wiedermeier et al., (1995).

Figure 3-1. Flow Chart for Evaluation of Intrinsic Remediation Potential at Petroleum Hydrocarbon Contaminated Sites (after Wiedermeier et al., 1995)


Review Available Site Data and Develop Preliminary Conceptual Model
Make Preliminary Assessment of Potential For Intrinsic Remediation and Engineered Remediation Based on Existing Site Characterization Data
Implement Other Protocols
Intrinsic Remediation
Does Intrinsic Remediation Alone Pass Initial Technical and Regulatory Screening?
NO
YES
Perform Site Characterization to Support Intrinsic Remediation
Refine Conceptual Model and Complete Pre-Modeling Calculations
Simulate Intrinsic Remediation Using Solute Fate and Transport Models
Use Results of Modeling and Site-Specific Information in and Exposure Pathways
Will Remediation Objectives Be Met Without Posing Unacceptable Risks to Potential Receptors?
NO
YES
Evaluate Use of Selected Additional Remedial Options Along with Intrinsic Remediation
Other
LNAPL Recovery
Pump & Treat
Bioslurping
Enhanced Bioremediation
Reactive Barrier
Air
Bioventing
Excavation
Perform Site Characterization to Support Remedy Decision Making
Assess Potential For Intrinsic Remediation With Remediation System Installed
Refine Conceptual Model and Complete Pre-Modeling Calculations
Simulate Intrinsic Remediation Combined with Remedial Option Selected Above Using Solute Transport Models
Use Results of Modeling and Site-Specific Information in an Exposure Assessment
Does Revised Remediation Strategy Meet Remediation Objectives Without Posing Unacceptable Risks To Potential Receptors?
NO
YES
Develop Draft Plan for Point -of-Compliance Monitoring Wells and Long-Term Monitoring
Present Findings and Proposed Remediation Strategy to Regulatory Agencies

The appendices to the document provide detail on site characterization techniques, processes affecting fate and transport of contaminants, data interpretation and calculations, and modeling the fate and transport of dissolved fuel hydrocarbons. The document also provides two case studies documenting the implementation of intrinsic remediation at Hill Air Force Base in Utah and Patrick Air Force Base in Florida. These case studies can be used by proponents as guides to data collection and evaluation.

3.2.2.3 American Society For Testing And Materials

The American Society for Testing and Materials (ASTM) has published a number of guides dealing with site investigation, risk based corrective action, and use of natural attenuation for petroleum hydrocarbons.

Guide E 1943, Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites, is a guide for determining the appropriateness of remediation by natural attenuation and implementing remediation by natural attenuation at a given petroleum release site, either as a stand alone remedial action or in combination with other remedial actions (ASTM, 1998). The Guide recognizes that natural attenuation can be used as a sole remedial action provided that immediate risks to human health, safety and the environment either do not exist or can be dealt with at the site in question. The Guide also spells out potential advantages and disadvantages of natural attenuation and stresses the need for monitoring to confirm that suspected processes associated with natural attenuation are working and that changes to site conditions do not alter their effectiveness.

Evaluation of natural attenuation is based on two primary lines of evidence: a stable or shrinking plume, and geochemical indicators of naturally occurring biodegradation and estimation of biodegradation rates. Fate and transport modeling and microbiological studies are seen as optional lines of evidence. The appendices to the Guide provide a thorough discussion of the evaluation of data collected to satisfy the primary lines of evidence. A discussion of each calculation is given and examples provided to assist the user in data interpretation.

The Guide lists the following as key components for decision making related to the use of natural attenuation:

- Site characterization and establishment of remedial goals
- Evaluation of plume status
- Comparing remediation by natural attenuation performance to remedial goals
- Comparing remediation by natural attenuation to other remediation options
- Development and implementation of an appropriate monitoring program

The guide indicates that site characterization must provide a proponent with enough information to determine if natural attenuation is a viable option for a site. This includes information on site geology, hydrogeology, contaminants of concern, sources and distribution of contaminants, migration pathways and receptors. A conceptual model showing potential exposure pathways to receptors should also form part of the site characterization. Remediation goals are to be determined using ASTM's *Standard Guide for Risk-Based Corrective Action at Petroleum Release Sites* (ASTM, 1995) and can be either concentration based target levels to be applied at specific points across the site or performance based criteria such as demonstrated containment of the plume.

Evaluation of plume status provides the primary evidence for judging effectiveness of natural attenuation at a site. Historical information on contaminant concentrations is seen as the best evidence in support of an evaluation. A shrinking or stable plume over time indicates that natural attenuation processes are effective in controlling and reducing migration and mass of contaminants respectively at a site. In situations where historical information is not available, options for providing evidence include monitoring to collect additional contaminant concentration data, collection and evaluation of geochemical data, and estimation of the natural attenuation rate.

Potential use of natural attenuation as a remediation option should include comparison with other remedial options. Natural attenuation should only be considered for a site if it can achieve the desired goals within the desired time frame, and it provides an acceptable level of risk or exposure prevention. Items such as cost-effectiveness and ability of natural attenuation to deal with land use changes should also be evaluated.

Once natural attenuation has been accepted for implementation, a monitoring program must be established for the site. The program must be able to evaluate performance and progress of natural attenuation towards meeting remedial goals and ensure that plume migration meets expected performance (ASTM, 1998). Monitoring frequency should be quarterly for the first year and then determined on a site-specific basis thereafter. Contingency plans must be implemented where monitoring information indicates that natural attenuation is not performing as predicted.

3.2.2.4 State of Alaska

The State of Alaska has its own formal policy on the use of natural attenuation as a remediation option for contaminated sites. In August, 1999, the Alaska Department of Environmental Conservation (ADEC) issued a revised draft of *Guidance on the Selection of Natural Attenuation as a Cleanup Alternative for the Restoration of Groundwater at Contaminated Sites* (ADEC, 1999). The necessity for and degree of cleanup required to protect human health, safety and welfare and the environment are established under Alaska's Contaminated Sites Remediation Program (18 AAC 75 Article 30). These regulations define site characterization requirements, soil, groundwater and surface water cleanup standards, and reporting and monitoring requirements for sites where discharges or releases have occurred.

ADEC does not consider natural attenuation to be a presumptive or default remedy. Natural attenuation is considered to be one option that may be evaluated along with other viable options during the site characterization phase. Natural attenuation should only be selected when it meets all relevant cleanup selection criteria, where it is fully protective of human health, safety and the environment, where it will meet site cleanup objectives, and where the time frame for cleanup will be reasonable compared to other options. Selection of natural attenuation must be supported by detailed site-specific information that demonstrates effectiveness of the approach. Use of natural attenuation does not imply that activities associated with investigating a site or selecting a remedy have been eliminated (ADEC, 1999).

Implementation of natural attenuation at a site is only allowed after several pieces of information are provided. These pieces of information are discussed below.

Site Characterization

Site characterizations for natural attenuation require a quantitative understanding of such things as:

- Source mass
- Groundwater flow
- Contaminant phase distribution and partitioning between soil
- Groundwater and soil gas
- Rates of biological and non-biological transformation
- How all these factors vary with time

Site characterization should include collecting data to define the nature and distribution of the contamination source(s), movement of contamination, and vertical and lateral extent of a groundwater plume and its potential impacts on receptors. A detailed understanding of aquifer hydraulics, recharge and discharge areas and volumes, and chemical properties is required to assess the contributions of adsorption, dispersion and dilution on natural attenuation of contaminated groundwater. Analytical or numerical simulation of complex attenuation processes should also form part of the site characterization process.

Process Efficacy

Once site characterization data have been collected, the next step is to evaluate efficacy of the natural attenuation process.

Three types of site specific evidence should be used in such an evaluation (ADEC, 1999):

- Historical groundwater and soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and concentration over time at appropriate monitoring or sampling points
- Hydrogeologic and geochemical data that can be used to demonstrate the type(s) of natural attenuation processes active at a site and the rate at which such processes will reduce contaminant concentrations to required cleanup levels
- Data from field or microcosm studies that directly demonstrate the occurrence of a particular natural attenuation process at a site and its ability to degrade contaminants of concern.

Appropriate Sites

In determining whether natural attenuation is an appropriate remedy for soil or groundwater, factors listed below should be considered by a proponent. These factors also constitute evaluation of potential effects to sensitive receptors, including:

- Whether contaminants present can be effectively remediated by natural attenuation processes
- Whether resulting transformation products present a greater risk than parent contaminants
- Whether nature and distribution of contaminant sources will allow them to be adequately controlled
- Whether a plume is relatively stable or is still migrating and the potential for environmental conditions to change over time

- Whether existing or proposed active cleanup measures will affect the natural attenuation component of the remedy
- Whether drinking water supplies, other groundwaters, surface waters, ecosystems, sediments, air or other environmental resources could be adversely affected as a result of selecting natural attenuation as the remediation option
- Whether a time frame for natural attenuation is reasonable compared to time frames for other remediation options
- Changes to demand for the affected aquifer over the duration of the natural attenuation process
- Whether site specific vehicles for implementing institutional controls such as deed restrictions are available and whether they are binding and enforceable
- Whether the natural attenuation remedy is in compliance with ADEC regulations in 18 AAC 75 Article 3

Reasonableness of Remediation Time Frame

Longer time frames associated with use of natural attenuation must be compatible with site-specific land and groundwater use. While it is expected that natural attenuation may require somewhat longer time frames for cleanup than other remediation options, those time frames should not be excessive when compared to those other options. Factors that should be considered when evaluating the length of time appropriate for remediation include:

- Classification of the type of groundwater resource and value of the resource
- Relative time frame in which affected portions of an aquifer might be needed for future water supply
- Uncertainties regarding mass of contaminants in the subsurface
- Reliability of monitoring and institutional controls over long time periods
- Public acceptance of the extended time for cleanup
- Provisions by a proponent for monitoring and performance evaluation over the period of time for cleanup

Consideration of these factors should allow ADEC to determine whether natural attenuation will fully protect human and ecological receptors and whether site cleanup objectives and the time frame needed to meet these objectives will be reasonable. ADEC also expects that source removal will form part of any proposal involving natural attenuation.

Performance Monitoring

Performance monitoring to evaluate effectiveness of natural attenuation is considered to be a critical part of a cleanup program. The monitoring program developed for a site should specify the location, frequency, and types of samples and measurements necessary to evaluate performance as well as define anticipated performance objectives. All monitoring programs should be designed to accomplish the following:

- Demonstrate that natural attenuation is occurring according to objectives and expectations specified in the monitoring work plan
- Demonstrate that geochemical conditions are conducive to natural attenuation processes
- Identify any potential toxic transformation products resulting from natural attenuation processes
- Determine if a plume is expanding
- Ensure no impact to downgradient receptors
- Detect new releases of contaminants to the environment that could affect the effectiveness of the natural attenuation remedy
- Detect changes in environmental conditions that may reduce the efficacy of the natural attenuation processes
- Verify attainment of cleanup levels

Performance monitoring is required as long as contamination remains above approved cleanup levels. Monitoring may also continue for a specified time after cleanup levels have been achieved to ensure that concentration levels are stable and remain below cleanup levels. A long-term monitoring plan must be submitted to ADEC as part of any proposed natural attenuation program.

Contingency Remedies

A contingency remedy is defined as a cleanup technology or approach that functions as a "backup" remedy in the event that the selected remedy fails to perform as anticipated (ADEC, 1999). Contingency remedies would be employed where natural attenuation is not proven for the site-specific application, where there is significant uncertainty regarding the nature and extent of contamination at the site, or where there is uncertainty regarding whether natural attenuation will perform as anticipated. The Guide also recommends that a number of triggers be established in the cleanup decision document that will signal unacceptable performance of natural attenuation at a site. These triggers could include when:

- Contaminant concentrations in soil or groundwater at specified locations exhibit an increasing trend
- Near source wells exhibit large concentration increases indicative of a new or renewed release
- Contaminants are identified in sentry/sentinel wells located outside of the original plume boundary, indicating renewed contaminant migration
- Contaminant concentrations are not decreasing at a sufficiently rapid rate to meet the approved cleanup levels
- Changes in land and/or groundwater use will adversely affect the protective capability of the natural attenuation remedy

3.2.2.5 State of Florida

The State of Florida's Department of Environmental Protection (FDEP) is responsible for regulating use of natural attenuation at contaminated sites. Natural attenuation is considered under Florida regulation Chapter 62-770 of the Florida Administrative Code

Petroleum Contaminated Site Cleanup Criteria (FDEP, 1997). This regulation defines assessment and cleanup procedures for petroleum contaminated sites. After 1997, FDEP's Bureau of Petroleum Storage Systems added a guidance document *BPSS-11, Natural Attenuation Evaluation Procedures* (FDEP, 1998) to supplement their treatment of natural attenuation. It is based on the draft ASTM procedure on natural attenuation.

FDEP has approved natural attenuation monitoring programs in its cleanup programs for several years in the form of monitoring only plans (MOPs). Criteria for MOPs are set out in Chapter 62-770 (FDEP, 1997). The criteria incorporate specific factors into the rule for determining if monitoring of natural attenuation is an acceptable remediation strategy. The requirements of the rule allow for two general procedures for justifying the use of natural attenuation as a remediation remedy.

The first procedure, described as a "Level 1 evaluation", allows for a simplified justification of natural attenuation as a remediation strategy. A Level 1 evaluation indicates that natural attenuation is appropriate for a site if the following criteria are met (FDEP, 1997):

- Absence of free product
- Absence of soil contamination or evidence that soil will not constitute a continuing contaminant source
- Groundwater contamination above background levels or regulator specified cleanup levels are not migrating beyond points of compliance
- Physical, chemical, and biological characteristics of contaminants are conducive to natural attenuation
- Natural attenuation is anticipated to remediate the site in five years or less

If the criteria of the Level 1 evaluation are not met, natural attenuation may still be considered as a remedy. However, a more rigorous demonstration of natural attenuation feasibility is required (FDEP, 1998).

A Level 2 evaluation comprises the following (FDEP, 1997):

- Technical evaluation of groundwater and soil characteristics, chemistry, and biological activity that verifies contaminants will degrade under site-specific conditions
- Scientific evaluation (historical data or modeling results) of the potential for plume migration to reach points of compliance
- Estimation of annual target concentration reduction of contaminants in groundwater monitoring wells
- Estimation of timeframe for remediation
- Comparison of projected costs for natural attenuation versus other remediation alternatives

The strategy for dealing with soil contamination exceeding soil cleanup target levels must be considered before embarking on a program of long-term monitoring of natural attenuation in groundwater. If soil contamination above target cleanup levels remains on site, the soil will have to be remediated, or alternatively, conditional closure may be issued by FDEP if the proponent is willing to agree to deed restrictions as an assurance that engineering and/or controls will remain in effect (FDEP, 1998). Even if the groundwater is ultimately remediated by natural attenuation to applicable groundwater target levels, final closure will only be issued if soil cleanup target criteria are also met. Once natural attenuation has been proven by either the Level 1 or Level 2 evaluation, annual milestones for contaminant concentration reductions in monitoring wells must be set.

Procedures for Verification of Natural Attenuation

The following procedures for verifying the occurrence of natural attenuation at a site came as a result of revisions to the petroleum cleanup program in January 1998 (FDEP, 1998). The revisions include comments made at a series of public meetings held between

January 1997 and February 1998. The verification procedures include the following (FDEP, 1998):

A. Examination of Historic Data

Historical data, if considered sufficient, can be used to examine the vertical and areal extent of a plume with time. The purpose is to determine if the plume is stable, shrinking or expanding. The evaluation must also determine decay rate kinetics as a function of time or distance for all contaminants of concern. The ASTM draft Standard *Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites* (ASTM, 1998) is referenced as an appropriate means of calculating decay rates. There is also a requirement for statistical and practical relevance of decay rate determination to be evaluated. If the decay rate is evaluated as a function of distance, the following support information is required:

- Groundwater flow direction must be defined
- Concentration data must be available from a minimum of three monitoring wells along the direction of groundwater flow
- Calculation of decay rate requires an estimate of groundwater velocity

B. Evaluation of Geochemical Indicators Supporting Natural Attenuation

In the absence of sufficient historical data, the verification procedure allows for a more aggressive approach to assess geochemical indicators used to demonstrate the effect of natural attenuation at a site. This assessment can also be used as an extra measure to support historical data review as discussed in item A above. Based on site assessment, representative monitoring wells indicating groundwater contamination, as well as a sufficient number of up and down gradient wells, should be sampled for chemicals of concern and all appropriate biological indicators (FDEP, 1998). Representative monitoring wells should be selected based on contaminant concentration distribution, areas of potential aeration such as drainage structures, monitoring well construction, and well location. Trends in concentration differences between background and contaminated area wells should be properly evaluated.

In areas where dissolved oxygen is above 1 to 2 mg/L, an assumption can be made that oxygen is the preferred electron acceptor. Biological indicators in that instance would include, as a minimum, dissolved oxygen and pH. In areas where dissolved oxygen is below 1 mg/L, biological indicators for anaerobic degradation should be included in a sampling program. Geochemical parameters would then include, as a minimum, sulfate, nitrate, iron, methane, manganese, redox potential and pH. Field measurements of these parameters are allowed. Indicators for biodegradation should be evaluated according to ASTM draft *Standard Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites* (ASTM, 1998) and a method for calculating theoretical biodegradation capacity is included in the Florida guidance document (FDEP, 1998).

C. Fate and Transport Modeling

For sites with complex conditions such as an expanding plume or multiple sources, all appropriate attenuation processes should be evaluated using a fate and transport model. FDEP maintains a list of acceptable models. Any and all input parameters must be fully justified by information obtained from a site or by sound technical assumptions. An error calculation must be made and it must fall within a scientifically acceptable range. Proper calibration of the model is expected where data are sufficient. Based on modeling, the time required to achieve no further action may be calculated. A cost evaluation of natural attenuation is also expected in comparison to other remediation methods.

D. Monitoring Requirements

I. Initial Year

In the absence of sufficient historical data, quarterly monitoring is expected. A representative number of source wells and a minimum of one downgradient well should be monitored. Monitoring parameters would include water table elevations, chemicals of concern and appropriate biological indicators.

II. Subsequent Years

Based on the initial year's data and the estimated time of cleanup, semi-annual or annual monitoring is required. Parameters would include those of the initial year.

Monitoring reports are to be submitted semi-annually for the first year and annually thereafter. Also required with the status reports is an updated evaluation of the modeling predictions.

3.2.2.6 State of Michigan

The Michigan Department of Environmental Quality (MDEQ) is responsible for regulating remediation of contaminated sites. There are four main documents dealing with site remediation and natural attenuation in the State of Michigan. They are:

- Part 201 of the Natural Resources and Environmental Protection Act (Act 451) of 1994 and revised in 1996 – *Environmental Remediation* (MDEQ, 1996)
- Part R299 – *Environmental Contaminant Response Activity*, 1990 (MDEQ, 1990)
- *Fundamental Principles of Bioremediation* (an aid to the development of bioremediation proposals), April, 1998 (MDEQ, 1998a)
- Interoffice Communication, *Relevant Information for Reviewing Proposals on Natural Attenuation through Unenhanced Bioremediation*, July, 1998 (MDEQ, 1998b)

The first two documents deal with general reporting, investigation, implementation and monitoring requirements for any type of release. These documents consider all forms of site remediation and do not specifically mention natural attenuation or bioremediation.

However, natural attenuation can be considered as a remediation option under these regulations.

Part 201 – *Environmental Remediation* (MDEQ, 1996).

This document lists the contents of, and procedures for, obtaining a remedial action plan and its approval. Any plan must be protective of human health, safety and welfare, and the environment. Cost effectiveness is considered when selecting and reviewing remediation alternatives. Remedial actions that permanently and significantly reduce the volume, toxicity, or mobility of hazardous substances are preferred (MDEQ, 1996). There are several objectives that can be achieved by a remedial action depending on degree of risk to receptors. One of the conditions is that remedial action provides for reduction of hazardous substance concentrations in an aquifer through a "naturally occurring process" that is documented to occur at a site. Natural attenuation is considered in the discussion of "naturally occurring process" (Stenzel, 1999). A proponent must submit a remedial action plan to MDEQ for approval prior to implementing the plan. A remedial action plan may be revoked by MDEQ if the proponent fails to maintain monitoring or if land use restrictions placed on a site at the time of implementation of the plan change. MDEQ requires the proponent to provide financial assurance to pay for monitoring, operation and maintenance of the remedial action as part of all remedial action plans.

Part R299 - *Environmental Contaminant Response Activity* (MDEQ, 1990).

Objectives of a response activity covered by this document are similar to those in Part 201 above, with the exception that source control or abatement measures shall be undertaken whenever feasible. Remedial action plans are to include an operation and maintenance plan, a monitoring plan, and any land use restrictions imposed on the site during completion of the response activities. Remedial actions that are naturally occurring biological or chemical processes that can be documented to occur at the site are allowed (MDEQ, 1990).

Both of the above documents deal with public participation in the remedial action plan development or implementation. Part 201 (MDEQ, 1996) requires a public meeting to discuss the investigation and proposed remedial action plan but only at sites where state funds will be spent on a site. Part R299 (MDEQ, 1990) allows for public meetings where Type C criteria (established by a site-specific risk assessment) are proposed for a site or for any site where MDEQ determines that there will be significant public interest.

Interoffice Communication – *Relevant Information for Reviewing Proposals on Natural Attenuation Through Unenhanced Bioremediation*, (MDEQ, 1998b).

This document is a concise summary of the protocols recommended in scientific literature for verification of natural attenuation through unenhanced bioremediation projects. Additional information on bioremediation processes is included in MDEQ document *Fundamental Principles of Bioremediation*, (MDEQ, 1998a).

MDEQ requires three lines of evidence to prove that the rate of bioremediation is adequate to protect public health and the environment:

- Observed reductions in contaminants along the plume flowpath
- Documented loss of contaminant mass using geochemical data and/or conservative tracer studies with a rigorous estimate of residence time
- Microbiological lab data to support, and give rates of, biodegradation

MDEQ recommends that a minimum of eight consecutive quarters of monitoring data be obtained. These data can be used to provide an historical perspective on degradation rates and to evaluate seasonal variations in the groundwater and its potential affect on the rate and success of biodegradation.

A minimum of six monitoring wells should be used with additional sites determined by the site's geology and hydrogeology. Samples are to be collected from the most contaminated part of the plume, downgradient of the source but within the plume, downgradient of the plume, and in background areas. Collected data should be used to model the site and gain further understanding of biodegradation processes.

Downgradient sentinel wells must form part of the monitoring program. These wells provide trigger points such that if remediation objectives are exceeded, the compulsory contingency plan can be implemented.

Once it has been determined that natural attenuation is occurring at a site, a long-term operation and maintenance plan must be developed. This plan details the sampling program used to determine that natural attenuation will be protective of human health and the environment.

3.2.2.7 State of Minnesota

Minnesota Rules Chapter 7060 *Minnesota Pollution Control Agency (MPCA), Water Quality Division, Underground Waters* establishes state policy and imposes regulations on pollution of all groundwaters in the state (MPCA, 1998a). The goal of the legislation is to preserve these groundwaters for their highest resource values defined as a drinking water, culinary or food processing water source. The health risk limits adopted under Minnesota Statutes Section 103H.201 (MPCA, 1994) are the appropriate cleanup levels for managing groundwater contamination and risk to human receptors.

MPCA has developed a working draft of a Groundwater Guidance Document (MPCA, 1998b). The intent of the guidance is to develop a consistent framework through which groundwater contamination issues are evaluated and remedial action decisions are managed in the state. The policy is to apply promulgated standards as cleanup levels, stabilize plumes which migrate through aquifers at concentrations which exceed cleanup levels, and implement remedial actions which manage the risk a groundwater plume poses to human health and the environment (MPCA, 1998b). Groundwater remedial actions are separated into two categories: interim response actions that control and eliminate exposure to contamination posing an immediate human or environmental receptor risk and actions that eliminate long-term risks to current and future receptors. Evaluating the degree of groundwater contamination and developing appropriate remedial activities involves a remedial investigation. Major activities in that investigation include a receptor survey, a hydrogeologic evaluation, groundwater flow modeling, development of an interim response action, and ultimately, the remedial action decision.

To assist with the consideration of natural attenuation as a remediation option for petroleum hydrocarbon contaminated sites, MPCA has issued Fact Sheet #3.21 *Assessment of Natural Biodegradation at Petroleum Release Sites*, dated May 1996 (MOCA, 1996). This document explains how to assess the occurrence of natural biodegradation where a petroleum release has impacted a resource aquifer (MPCA, 1996). According to the fact sheet, an evaluation of bioactivity at a site involves analysis of groundwater samples for pertinent inorganic parameters such as dissolved oxygen, soluble ferrous iron and sulphate, establishment of a monitoring well network, and data analysis. The fact sheet indicates that an adequate monitoring network for natural attenuation will require:

- One well near the source of the release
- Several wells along the longitudinal axis of the contaminant plume
- One background well
- Several wells along the outer boundary of the contaminant plume

Results of data analysis should establish a difference of relative electron acceptor concentrations or metabolic byproduct concentrations inside versus outside a plume. To evaluate occurrence of natural biodegradation, concentrations of the following inorganic parameters should be measured both inside and outside a plume (MPCA, 1996):

- Dissolved oxygen
- Nitrate
- Soluble ferrous iron

- Sulphate or sulphide

Calculation of a contaminant reduction rate as part of the bioactivity evaluation is seen as optional but is recommended for plumes more than 61 metres in length. The fact sheet discusses a concentration versus distance approach for its calculation. This approach uses groundwater monitoring data for BTEX to estimate the contaminant reduction rate. It requires data from two or more wells located close to the longitudinal axis of the plume, beyond the presence of free product and far enough apart that BTEX concentrations differ by several fold. The reduction rate is calculated by:

$$k = (-\ln(C_z/C_y))V_p/x \qquad (15)$$

Where: k = first order decay constant (day^{-1})

C_y = concentration of BTEX in a well near the source (μg/L)

C_z = concentration of BTEX in a well further away from the source (μg/L)

V_p = plume velocity (m/day)

x = distance between wells (m)

The reduction rate is assumed to be first order and is used to assist a proponent in deciding whether to monitor only or to implement some more active form of remediation.

MPCA has also issued a working draft for natural attenuation of chlorinated solvents *Natural Attenuation of Chlorinated Solvents in Groundwater,* dated December 12, 1997 (MPCA, 1997). The document gives guidance on selection of natural attenuation as a remediation option for groundwater contaminated with chlorinated solvents. The selection process is a two-phased approach involving an initial screening and detailed site characterization.

The initial screening phase involves sampling monitoring wells at locations background to and within a plume. Samples are analyzed for a range of organic and inorganic parameters, both in the field and lab, which indicate whether the oxidation/reduction state of groundwater is favourable to natural attenuation processes. Results from the analytical program are used to assess the oxidation/reduction state of the site by awarding points in a ranking system for those analytes that indicate reducing conditions in groundwater. A score of 0 to 5 points indicates inadequate evidence for natural attenuation. A score of 6 to 14 points indicates limited evidence. A score of 15 to 20 indicates adequate evidence and a score of >20 points indicates strong evidence. MPCA suggests that a score of <15 points does not warrant pursuing natural attenuation as a remediation option. Preliminary modeling as part of the screening process provides an early indication as to whether natural attenuation is a promising solution for a site. Using a tool such as Bioscreen allows for comparison between the distance groundwater contamination is likely to move without assuming biodegradation or attenuation versus the distance when degradation factors are incorporated into the model.

The second phase consists of a detailed site characterization that could be compared to a feasibility study. The characterization includes refining site specific biodegradation rates, obtaining detailed hydrogeologic data, plume definition, exposure pathways, and distances to receptors. Fate and transport modeling is used to refine predictions made regarding plume behavior over time.

Implementation of natural attenuation includes placement of monitoring wells between the plume edge and exposure points, establishing a long-term sampling plan, and establishment of contingency plans in the event of unforeseen plume expansion. Regardless of the potential success of natural attenuation as a remediation option, MPCA recommends that the contaminant source be removed.

The guidance also provides a workplan checklist for natural attenuation based on the USEPA technical protocol for evaluating natural attenuation for chlorinated solvent contaminated groundwater (USEPA, 1998).

3.2.2.8 State of Utah

The State of Utah's Department of Environmental Quality (UDEQ) issued a final draft of its Tier 2 Risk Based Corrective Action document *Guidelines for Utah's Corrective Action Process for Leaking Underground Storage Tank Sites* on July 30, 1999 (UDEQ, 1999). The document was developed using USEPA, ASTM and DOD policies and protocols and with the assistance of representatives from industry and consulting companies. It describes a process to evaluate risks to human health and the environment due to petroleum hydrocarbon contamination from leaking underground storage tanks. The process is intended to address cleanup when maximum contaminant levels or other applicable cleanup standards cannot reasonably be achieved.

Utah uses a modified ASTM two-tiered approach for performing risk assessments. Initially, a Tier 1 screening analysis is performed using general Utah-specific hydrogeological data and standard exposure assumptions to estimate screening level concentrations at a source area. These initial source area Tier 1 screening levels are expected to attenuate to maximum allowable concentrations within specific critical distances from the source area. Critical distances are specified for items such as utility lines, property lines, buildings, water wells and surface water in Utah's *Guidance for Tier 1 Risk-Based Corrective Action, 1997* (UDEQ, 1997). If the screening levels are exceeded at the critical distance, then the proponent has the option to clean up to applicable standards or to perform a Tier 2 risk assessment to determine if receptors are protected. A Tier 2 assessment first requires the proponent to complete a subsurface investigation to determine soil and groundwater impacts and associated exposure pathways. Details on the components of a subsurface investigation are provided in Utah's *Leaking Underground Storage Tank (LUST) Subsurface Investigation Report Guide,* April 1998 (UDEQ, 1998). Once the investigation is complete, the proponent can either prepare a corrective action plan or a Tier 2 risk assessment proposal to further define corrective action plan requirements.

The Tier 2 risk assessment incorporates a natural attenuation factor. The natural attenuation factor is used to calculate site specific cleanup levels for each exposure pathway and contaminant of concern. Natural attenuation factors can be calculated either by empirical methods based on the measured concentration ratio between source and points of exposure or estimated based on fate and transport modeling to predict concentration reductions between source and points of exposure.

For each exposure pathway posing a potential concern, the proposed corrective action plan must achieve minimum performance standards. Therefore, appropriate corrective action depends on the immediacy of exposure. For example, UDEQ considers that all groundwater must be protected as a potential drinking water resource (UDEQ, 1998). A corrective action must be able to preserve that potential groundwater resource to quality conditions suitable for human consumption. Corrective action involving active removal or treatment of contaminated soil or groundwater may be required to deal with present day exposures whereas passive corrective action such as natural attenuation may be all that is required for future potential exposures.

The corrective action plan must evaluate appropriate and applicable remediation alternatives on the basis of technical feasibility, cost-effectiveness and ability of the method to protect human health and the environment. Once the corrective action plan or risk assessment has been completed, the proponent is required to submit information confirming that the applicable standards have been achieved. In the case of natural attenuation, this information must demonstrate that controls will prevent human exposure to harmful levels of the contaminants of concern. Any corrective action involving groundwater requires sampling and compliance monitoring for a period specified by the regulator. This monitoring is usually done on a quarterly basis.

3.2.2.9 State of New Hampshire

The State of New Hampshire Department of Environmental Sciences (NHDES) has two main Administrative Rules dealing with investigation, reporting and remediation of releases to soil and groundwater. They are Rule Env –Ws 412 *Reporting and Remediation of Oil Discharges* (NHDES, 1996), and adopted Rule Env-Wm 1403 (formerly 410) *Groundwater Management and Groundwater Release Detection Permits* (NHDES, 1993). In October 1998, New Hampshire also published *Draft Guidelines for Selection of Natural Attenuation for Groundwater Restoration* (NHDES, 1998) which are guidelines dealing with selection, reporting, and monitoring requirements for natural attenuation. The latter document also provides groundwater quality standards that must be met when site remediation is undertaken. Each of these documents will be discussed in some detail below.

Rule Env-Ws 412

This Rule, adopted on November 20, 1996, deals with reporting and remediation of oil discharges. Any person who discharges oil above a specified volume must report it to the NHDES and take steps to remediate the discharge. Any free product must be removed. The Rule also provides an outline of information required for site characterization to define the degree and extent of the contamination. Site characterization must include the following information:

- Data on the nature, location, and estimated quantity of the discharge
- Data from available sources or other investigations concerning:
  - Surrounding populations
  - Water quality
  - Use and approximate locations of drinking water supplies potentially affected by the discharge
  - Subsurface soil conditions
  - Locations of underground utilities, drains, and sewers
  - Land use
- Documentation of free product removal
- Preliminary assessment of receptors and potential receptors

This initial site characterization is followed by a specific site investigation to refine information previously provided. Once NHDES is satisfied with a site investigation, a remedial action plan (RAP) must then be submitted.

Site closure with no restrictions is achieved when health hazards and sources of contamination have been eliminated, when groundwater standards are met, and when liability requirements for cost of remediation have been met.

Rule Env-Wm 1403

Rule Env-Wm 1403 provides a broader perspective on the requirements for investigating, remediating and managing contamination for sites where discharges of regulated contaminants have occurred and to establish procedures for monitoring groundwater for early detection of any impact associated with regulated activities (NHDES, 1993). This rule, originally Env-Wm 410, was amended and adopted on February 11, 1993.

As with Rule Env-Ws 412, Rule Env-Wm 1403 specifies steps for reporting, investigating and remediating discharge to groundwater. However, this rule provides an expanded version of requirements for site characterization as well as ambient groundwater criteria that must be met during remediation. These ambient criteria do not apply to naturally occurring contaminants.

Requirements for site investigation and types of information required for site investigation reports are much more comprehensive in this document. Details on physical features of a site, facility features, site geology, sampling methods, and RAP must all form part of the report submitted to NHDES. The report must also contain a conceptual model of the site upon which decisions for site monitoring and remediation are based. The RAP must be submitted to NHDES within 120 days of approval of a site investigation report unless NHDES decides that no remediation is necessary. NHDES must approved the RAP before it can be implemented (NHDES, 1993).

Upon completion of the remedial action, NHDES issues two types of certificates. A Certificate of Completion is issued if the activities specified in the RAP, with the exception of soil and groundwater monitoring, have been met. Once monitoring has been completed and NHDES is satisfied that all human health hazards have been eliminated and that groundwater criteria have been met, a Certificate of No Further Action can be issued.

Draft Guideline for Selection of Natural Attenuation for Groundwater Restoration

Specific to natural attenuation, NHDES issued draft guidelines for selection of natural attenuation (NHDES, 1998) for restoration of groundwater contaminated with volatile organic compounds above ambient groundwater standards listed in Env-Wm 1403. The policy does not apply to contamination due to inorganic compounds or to contamination in the unsaturated zone. Reference is made throughout the guideline to related portions of Rule Env-Wm 1403. Officially, NHDES encourages the use of natural attenuation of dissolved phase contamination at sites where:

- It is demonstrated to be protective of human health and the environment and meets other relevant requirements of Env-Wm 1403
- It is demonstrated to present no additional risk to receptors
- A clear decreasing trend exists over time and distance for all regulated contaminant concentrations, including all regulated contaminant breakdown products
- Biodegradation or other destructive processes are demonstrated to be occurring
- Evidence of a stable or receding plume is provided
- Remedial goals will be achieved within a reasonable period of time including reduction of groundwater contaminant concentrations below ambient groundwater quality standards

NHDES does not approve site investigations or RAPs proposing natural attenuation without adequate site specific supporting data. Supporting information includes adequately characterized site hydrogeology, contaminant pathways, and estimates of travel times. NHDES also does not support natural attenuation as a stand-alone option if phase separated product or other contaminant sources are not controlled such that the source continues to add contaminant mass to the groundwater. In those instances, source removal is encouraged unless it can be demonstrated that the effects from the source are short term. Any proposal for natural attenuation must include a contingency plan should natural attenuation not achieve remedial goals.

Evidence for demonstrating effectiveness of natural attenuation can include information on historical trends, terminal electron acceptor (TEA) and byproduct concentrations, determination of rates of individual processes, quantitative evaluation of geochemical data, and microbiological evidence for occurrence of remediation processes. NHDES accepts three lines of evidence for natural attenuation. Primary evidence is to be evaluated for all sites where natural attenuation is proposed. It is to include evaluation of contaminant, TEA, and byproduct concentration trends over time in individual wells and over distance near a plume centerline, unaffected by human intervention. Acceptable primary evidence must clearly demonstrate that destructive processes are occurring. Secondary evidence must include evaluation of the rate of natural attenuation using appropriate analytical or numerical modeling or graphical methods. Secondary evidence may be required where historical trend data are unavailable or where a better understanding of the natural attenuation process is required. Microcosm studies may be accepted if the primary or secondary evidence is not sufficient or satisfactory. Recommended sampling and analysis procedures and appropriate analytical models are specified in the guidelines.

Remediation time is the predicted time needed to restore groundwater quality to achieve remedial goals (NHDES, 1998). This time must be reasonable based on site-specific criteria including the proximity and presence of receptors, aquifer use, contaminant characteristics, site geologic and hydrogeologic conditions, and use of institutional controls. NHDES uses a default time period of ten years as an acceptable remediation time. It does allow the time period to be increased or decreased based on information contained in a site investigation report or the RAP. Changes to the ten-year period must address the following:

- Resource value of affected groundwater, considering present and anticipated future uses
- Time frame in which portions of an aquifer might be needed for future water supply, considering the possibility of alternate supplies
- Uncertainties regarding contaminant mass, reactions, and fate and transport assumptions
- Reliability of monitoring and institutional controls (such as a record of a groundwater management zone on the deed)
- Comments from the public regarding remediation time
- Ability of a proponent to fund monitoring and evaluation over the remediation time period

Annual reporting is required unless directed otherwise by NHDES. The reporting must include all monitoring data, an evaluation of plume status, and an assessment of effectiveness of natural attenuation in meeting performance goals. Monitoring and reporting must continue at a site until remedial objectives for a site are met. A Certificate of No Further Action can be issued when it is demonstrated that there is no active contaminant source at the site, that there is an overall decreasing trend in volatile organic concentrations in groundwater, and that ambient groundwater quality standards have been met for at least two consecutive sampling rounds.

3.2.2.10 State of Texas

Remediation of contaminated sites in the State of Texas falls under jurisdiction of the Texas Natural Resource Conservation Commission (TNRCC). The Texas Water Act specifies the need to remediate sites where soil and groundwater have become contaminated. Guidance RG-261 *Operation, Monitoring and Performance of Remedial*

Systems (TNRCC, 1996a), lists many natural attenuation indicators that can be evaluated to determine if natural attenuation is occurring at sites. Responsible parties may include collection of natural attenuation indicator information in proposals to verify plume stability or propose use of monitored natural attenuation as a corrective action plan. Guide RG-41 *Corrective Action Plans for LPST (Leaking Petroleum Storage Tank) Sites* (TNRCC, 1996b), provides additional guidance for developing a corrective action plan.

The Texas Water Act provides a methodology for establishing criteria by which concentrations are determined for cleanup of leaking storage tank site releases. Concentrations are established for compliance points which are between the source area and potential exposure points. At the compliance point, concentrations must be at or below the established concentration. Institutional controls may be used as an exposure limiting measure when determining applicable criteria. For contaminants other than those released from underground storage tanks, the Act specifies information and procedures to demonstrate compliance with one of three risk reduction standards.

Risk reduction Standard 1 relates to closure or remediation to background levels. To obtain closure, the proponent must provide a final report that documents attainment of the risk reduction standard (remediation to background levels) in the exposure pathway media of concern. The report must include:

- Descriptions of procedures and conclusions of an investigation to characterize the nature, extent, direction, rate of movement, volume, composition and concentration of the contaminants in environmental media
- Basis for selecting the environmental media of concern
- Documentation supporting selection of exposure factors
- Description of removal or decontamination procedures performed in closure or remediation
- Summaries of sampling methodology and analytical results which demonstrate that contaminants have been removed or decontaminated to applicable levels

The basic criteria for closure for groundwater pathways are a stable or shrinking plume.

Risk reduction Standard 2 relates to closure or remediation to health-based standards and criteria. Cleanup levels are represented by Texas or USEPA promulgated health-based standards. In the absence of these standards, proponents must develop cleanup levels using procedures specified in the Texas Water Act. The reporting requirements for Standard 2 sites are similar to those of Standard 1 sites.

Risk reduction Standard 3 relates to closure or remediation without controls. In addition to the report required for Standards 1 and 2, the proponent must also conduct a risk assessment that describes potential adverse effects under both current and future conditions caused by release of contaminants in the absence of any actions to control or to mitigate that release.

The February 10, 1997 memorandum *Closure Process for Petroleum Hydrocarbon LPST Sites Exceeding Target Concentrations* (TNRCC, 1997) highlights situations where natural attenuation should be evaluated as a remedial alternative for groundwater contamination. A study of benzene plumes at underground storage tank sites by the Texas Bureau of Economic Geology concluded that 96% of plumes were stabilized or declining and that 86% of those plumes had concentrations that were stable or declining (Mace et al., 1997). This was seen as evidence that plumes were generally contained and degraded by natural attenuation conditions.

Decisions regarding use of natural attenuation at a site are based primarily on the concept of risk. Groundwaters with a low probability of future use have a low risk of future exposure. Therefore, if a current exposure risk does not exist via the groundwater pathway, then it is unlikely that future exposure risk will occur from the presence of longer-term contamination associated with remediation by natural attenuation.

Assessment of the feasibility of natural attenuation focuses on identification of sites where future exposure potential is low. These sites are classed as priority 4.1 and 4.2 sites. Priority 4.2 sites are those where only soils are affected, where target soil concentrations for human health have been met, where there are no surface waters within

150 metres, and where an outside municipal water supply is available. Priority 4.1 sites also meet these criteria but in addition may have affected groundwater. Institutional controls may be employed to provide a reasonable assurance against future exposure where exposure may otherwise occur. Figure 3-2 indicates which sites may be appropriate for a natural attenuation solution.

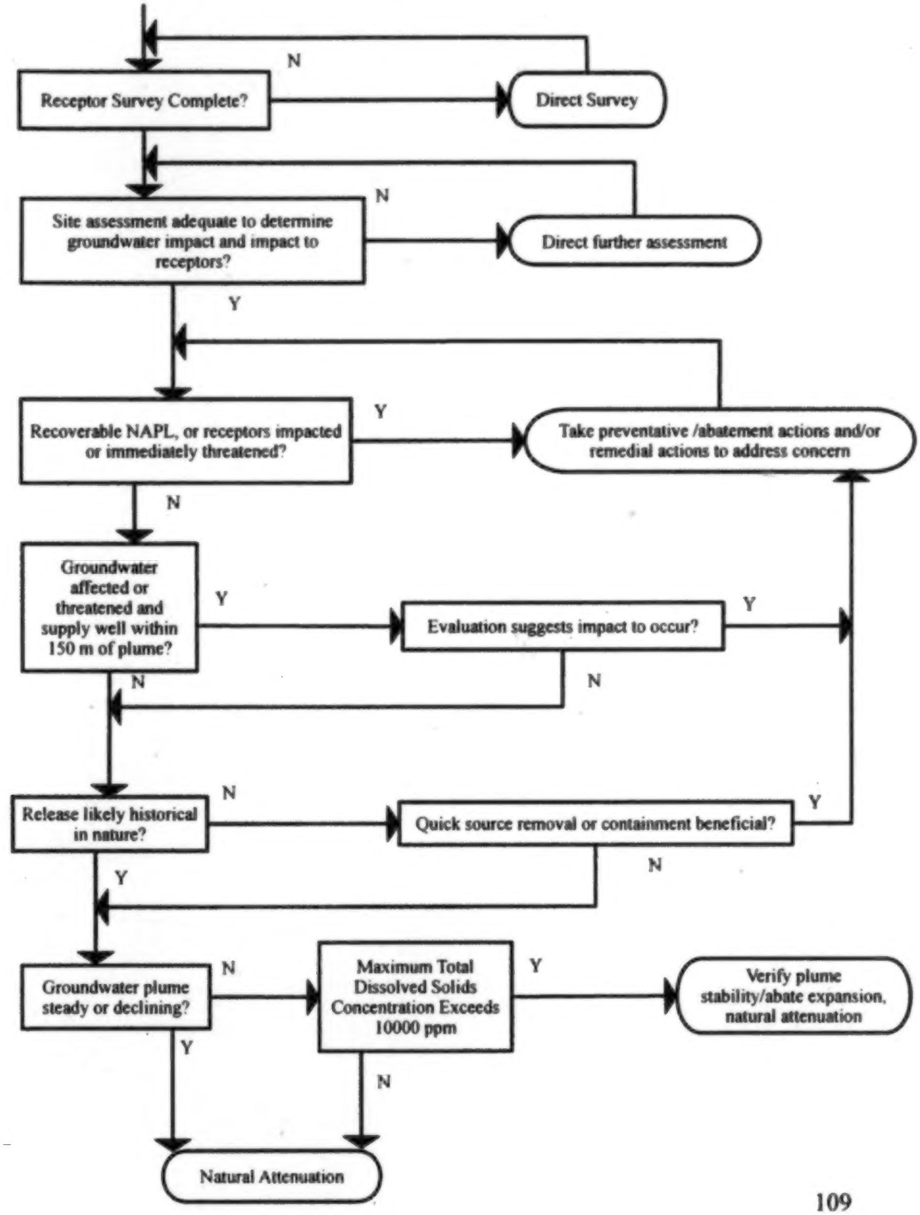
A proponent must supply the following information when seeking consideration of natural attenuation at a site (the "site" refers to all onsite and offsite affected properties) (TNRCC, 1997):

- Receptor survey and assessment of probable impact
- Adequate site characterization information
- Evidence of a stable or declining contaminant plume. This may be evaluated as the trend in concentration over time or by evaluating isoconcentration maps. Four monitoring events may be required to complete this evaluation
- Evaluation of potential future use of groundwater. This can also involve evaluation of wellhead protection zones for municipal supplies and future supplies

3.2.2.11 State of Wisconsin

Regulation of remediation of contaminated sites in the State of Wisconsin falls under jurisdiction of the Wisconsin Department of Natural Resources (WDNR). Relevant legislation in the State of Wisconsin related to site remediation requirements includes Chapter NR 140 (WDNR, 1996) and Series 700 (WDNR, 1997a) of the Wisconsin Administrative Code, the Hazardous Substance Spill Law, section 292.11 (WDNR,1997b) the Environmental Repair Statute, section 292.31 (WDNR, 1997c) and the Groundwater Law, subsections 160.23 and 160.25 (WDNR, 1984). Chapter NR 140 was first developed in 1985 and is essentially Wisconsin's Groundwater Quality Code. It lists groundwater performance standards in the form of preventative action limits and enforcement standards which, if exceeded, result in the requirement that groundwater

Figure 3-2. State of Texas Criteria for Natural Attenuation Preference for Petroleum Hydrocarbons at Leaking Petroleum Storage Tank Groundwater Sites (after TNRCC, 1997).


Receptor Survey Complete?
N
Direct Survey
Site assessment adequate to determine groundwater impact and impact to receptors?
N
Direct further assessment
Y
Recoverable NAPL, or receptors impacted or immediately threatened?
Y
Take preventative /abatement actions and/or remedial actions to address concern
N
Groundwater affected or threatened and supply well within 150 m of plume?
Y
Evaluation suggests impact to occur?
Y
N
N
Release likely historical in nature?
N
Quick source removal or containment beneficial?
Y
N
Y
Groundwater plume steady or declining?
N
Maximum Total Dissolved Solids Concentration Exceeds 10000 ppm
Y
Verify plume stability/abate expansion, natural attenuation
Y
N
Natural Attenuation

quality must be restored in a reasonable time frame. Revisions to Chapter NR 140 in November, 1996 specifically identify natural attenuation as one of the remedial options that may be selected to achieve quality restoration. Chapters NR 700 – 758 include all steps, criteria and requirements for the site investigation, remedy selection and remedy implementation phases of the case closure process.

Wisconsin has published two guidance documents related to natural attenuation and its applicability as a remediation option. The first, *Naturally Occurring Biodegradation as a Remedial Action Option for Soil Contamination – Interim Guidance (Revised)* (WDNR, 1994) was developed by the Emergency and Remedial Response Program. It emphasizes biodegradation of petroleum hydrocarbon contamination in the unsaturated zone but is considered applicable to other contaminants and to groundwater contamination (WDNR, 1994). While not comprehensive, this guidance document does discuss situations where natural biodegradation may be appropriate, requirements for site and process characterization, monitoring requirements, and reporting and documentation requirements. The second, *Interim Guidance for Selection of Natural Attenuation for Groundwater Restoration and Case Closure* under Section NR 726.05(2)(b) (WDNR, 1997d) was published in March 1997 by the WDNR Bureau for Remediation and Redevelopment. The purposes of these documents are to discuss selection of natural attenuation to restore contaminated groundwater and to discuss criteria that demonstrate when natural attenuation is effective and acceptable as a final groundwater remedy (WDNR, 1997d). The guidance provides information on requirements for site characterization, qualitative criteria such as proximity of receptors for assessing the feasibility of natural attenuation as well as monitoring and closure requirements.

Naturally Occurring Biodegradation as a Remedial Action Option for Soil Contamination – Interim Guidance (Revised) (WDNR, 1994).

In this document, "naturally occurring biodegradation" means degradation of organic compounds by indigenous microorganisms without artificial enhancement (WDNR, 1994). Wisconsin recognizes that this process may be a long-term process that may be acceptable provided impacts from site contamination are minimal. In discussing sites where naturally occurring biodegradation (NOB) may be acceptable, the guidance discusses factors such as:

- Magnitude, toxicity, and mobility of contaminants
- Proximity of human and environmental receptors, especially sensitive receptors and habitats
- Proximity of private and public water supplies
- Potential future use of an aquifer in the vicinity of a site
- Reliability and enforceability of institutional controls

These factors must be assessed and reviewed when determining the feasibility of NOB. In recognizing sites where NOB may be applicable, the guidance lists three acceptable scenarios. The first scenario is at low or medium priority sites where contamination is confined to unsaturated soils and levels of contamination are sufficiently low so that groundwater quality is not threatened. The second scenario is as a second phase of remediation after an active remediation process has been employed to sufficiently reduce contaminant concentrations to levels where migration to the groundwater would not violate Chapter NR 140 standards. The third scenario is at sites where groundwater contaminant concentrations are low level. Thorough site characterization is required in all scenarios but particularly in the third.

Site characterization discussed in this guidance document is in addition to site investigation performed in accordance to *WDNR Guidance for Environmental Response Actions*, March, 1992 (WDNR, 1992). Characterization for NOB involves identifying contaminants on site, assessment of physicochemical conditions and presence of appropriate nutrients and, in some cases, assessment of microbiological parameters to determine presence and viability of an appropriate microbiological population (WDNR, 1994).

Contaminant characterization involves not only defining types, amounts and extent of contaminants, but also biodegradability and microbiological degradation pathways for the contaminants identified. In situations where daughter products of degradation such as vinyl chloride from the metabolism of TCE are considered significantly more toxic than the parent contaminant, NOB may not be considered acceptable.

Site characterization involves a determination of whether physical and chemical conditions present at a site are favourable for biodegradation to occur. However, specific parameters required for adequate site characterization must be determined on a site-specific basis. The guidance document lists a wide range of parameters that may need to be evaluated and provides some discussion on the importance of a select number of those parameters. The list of parameters is shown in Table 3-5.

Table 3-5. Wisconsin Department of Natural Resources Suggested Soil and Groundwater Monitoring Parameters for Evaluation of Natural Attenuation Potential (WDNR, 1994).

• soil moisture content	• organic matter content (OMC)
• soil water holding capacity/field	• total organic carbon (TOC)
• capacity	• total organic nitrogen (TON)
• porosity	• redox potential (Eh^0)
• permeability	• inorganic nitrogen (as NH_3, NO_2, NO_3)
• bulk density	• soluble phosphorous (o-PO_4)
• soil temperature	• "soluble" manganese (Mn^{2+})
• soil pH	• iron (Fe^{2+}, Fe^{3+})
• soil water dissolved oxygen	• sulfate (SO_4^{2-})
• soil gas oxygen content	• exchangeable cations
• soluble potassium	• buffer index
• soluble salts	• Na, Ca, Mg, S, B, Cu, Zn
• cation exchange capacity (CEC)	

The guidance document recognizes that not all of these parameters need to be measured directly and can be estimated from other measured parameters.

Microbiological characterization involves enumeration of total aerobic heterotrophs and total hydrocarbon degraders. Enumeration can take place either in the field or the lab and samples for evaluation should be obtained from the contaminated site and background locations for comparison and evaluation. Documentation requirements for each type of characterization are discussed in the guidance document.

A monitoring plan must be developed and submitted as part of the plan of action. The plan must include (WDNR, 1994):

- Description of monitoring approach(es) and technique(s) to be used
- Description of sampling plan
- Analytes to be sampled
- Analytical methods to be used

WDNR recommends that sampling be done quarterly for the first year of a program and annually thereafter at the discretion of the WDNR project manager. It is recommended that nutrient sampling be repeated after five years. A variety of biodegradation monitoring approaches and techniques are allowed or are considered by WDNR. These include change in concentrations of original contaminants, change in concentration of co-reactants, soil gas monitoring, soil borings, and pore water sampling, and groundwater monitoring.

Interim Guidance for Selection of Natural Attenuation for Groundwater Restoration and Case Closure under Section NR 726.05 (2)(b) (WDNR, 1997d).

In this guidance document, natural attenuation is defined as reduction in concentration and mass of a substance and its breakdown products in groundwater, due to naturally occurring physical, chemical and biological processes without human intervention or enhancement. These processes include, but are not limited to, dispersion, diffusion, sorption and retardation, and degradation processes such as biodegradation, abiotic degradation and radioactive decay" (WDNR, 1997d). The guidance document was prepared under the assumption that closure was the ultimate goal of site remediation of contaminated groundwater. It was designed to assist proponents with providing sufficient information to prove that natural attenuation is an effective and final remedy for contamination that will allow for closure to be issued for a site. The guidance document provides details on site characterization, remedial option plan content (including feasibility studies), remedy selection (based on the above), remedial plan implementation, monitoring and site closure. The document also provides a table of acceptable soil, soil gas, and groundwater analytical protocols and standards.

Site characterization requirements are very similar to those required under the Groundwater Quality regulations (WDNR, 1997a). However, greater emphasis is placed on thoroughly defining migration pathways and site hydrogeological characteristics. Emphasis is also placed on a proponent ensuring that all remedial options are considered as information is gathered. Only when information clearly indicates that natural attenuation will address all migration pathways should further information be gathered to support this option. In cases where interim measures are required to prevent further migration of contaminants before natural attenuation can be implemented, those measures must be complete before natural attenuation is considered acceptable.

Data gathered at a site are to be used to assess what remedial option or combination of options will be effective in removing contamination and bringing the site to closure. When evaluating natural attenuation as a potential remedy, several factors should be considered, including the technical and economic feasibility of the option and the need to comply with all applicable environmental laws and standards (WDNR, 1997d). The technical feasibility study, which forms part of the remedial option plan, must take into account short and long term effectiveness of the remedial option, its ability to be implemented at a site, and projected site-specific time periods in which remediation to applicable standards will occur. Short and long term effectiveness is related to the degree to which toxicity, mobility, mass and concentration of contaminants is reduced, and the effectiveness of remedial option(s) in protecting public and environment during the time frame in which remediation is implemented. The length of implementation of the remedial plan must take into account future land use planning and its effect on items such as increased groundwater demand or the ability to maintain an effective groundwater monitoring program.

The guidance document requires that remediation take place in a reasonable amount of time. Several factors must be assessed when determining what is a reasonable amount of time. These factors include:

- Proximity of contamination to receptors
- Presence of sensitive receptors
- Presence of endangered species or habitats
- Current and potential uses of an aquifer, including proximity to private and public water supplies
- Magnitude, mobility and toxicity of contamination
- Geologic and hydrogeologic conditions
- Effectiveness, reliability and enforceability of institutional controls
- Naturally occurring biodegradation processes are reducing total mass of contaminants in an effective and timely manner

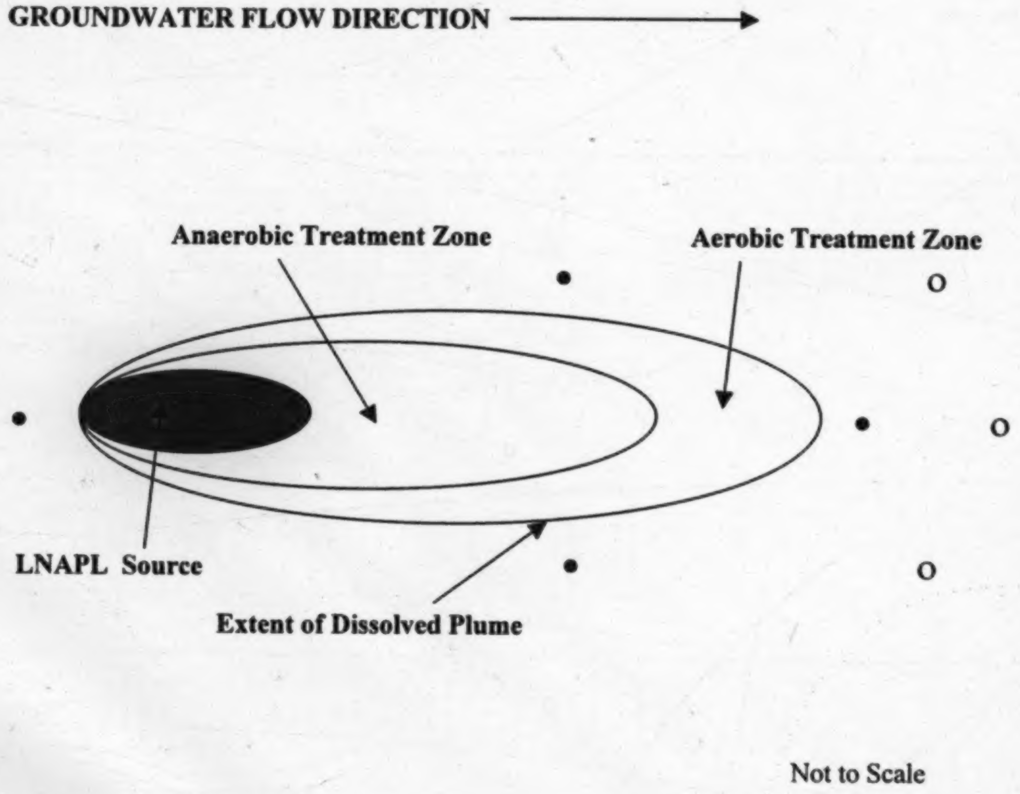
The purpose of considering such factors is to ensure that threats to receptors are not present, potential human or natural effects to plume migration are understood, processes for natural attenuation to occur are happening as predicted, and they are effective. The guidance document recognizes that natural attenuation alone may not be able to reduce soil or groundwater contamination within the required reasonable time. However, allowances are made for supplemental remedies to be employed which will reduce contaminant mass and afterward allow natural attenuation to achieve required remediation goals. Proponents are encouraged to contact local municipalities regarding future land use or aquifer use plans to ensure that natural attenuation fits with proposed development of areas adjacent to contaminated sites.

Economic feasibility must also form part of the remedial option plan. The costs of natural attenuation must be compared to the costs of all other viable remedial options. Potential future liability must also be considered as part of an economic feasibility study. As natural attenuation will be relied upon to continue remediating groundwater long after the site is closed, the proponent and the current landowner (if different) must be aware of site and surrounding natural and anthropogenic condition changes that may disrupt natural attenuation processes (WDNR, 1997d). If changes, such as surrounding land use, render natural attenuation no longer effective or introduce unacceptable risk such that a site is re-opened by WDNR, additional measures to remove that risk may be required.

A groundwater monitoring program, required as part of the technical feasibility study, must include sufficient groundwater monitoring wells, both in number and location, to measure groundwater flow direction(s), horizontal and vertical gradients and velocities, trends in contaminant concentration within the plume and source areas, and allow a judgement of whether a plume is migrating or presenting a threat to human health or the environment (WDNR, 1997d). An idealized monitoring strategy as suggested by the guidance document (WDNR, 1997d) is presented in Figure 3-3.

The typical monitoring scheme recommended by the guidance document (Figure 3-3) includes upgradient wells outside the plume to detect changes in background water quality. Sampling of these wells would include geochemical parameters and detected contaminants. The geology and hydrogeology of the site would determine the frequency of monitoring. For example, sites with coarse-grained soils may require more frequent monitoring. The upgradient monitoring can also be used in cases where there may be offsite contaminant source areas, to evaluate geochemical data and determine if electron acceptors are being depleted prior to reaching the onsite plume. Wells should be completed within the plume to provide data for trend analysis of contaminant concentrations with time. An ideal site would have these wells located along the centerline of the plume. Downgradient wells located outside of the plume would be used to detect potential continued migration of the plume. The number and locations of these

Figure 3-3. Wisconsin Department of Natural Resources Idealized Groundwater Monitoring Strategy for Natural Attenuation Sites (after WDNR, 1997).


GROUNDWATER FLOW DIRECTION
Anaerobic Treatment Zone
Aerobic Treatment Zone
LNAPL Source
Extent of Dissolved Plume
Not to Scale

LEGEND

- ● Long-Term Monitoring Well
- O Sentinel Monitoring Well

wells would be determined by site geology and hydrogeology, nature of the contaminants, and configuration of the plume.

Types of geochemical parameters are include dissolved oxygen, nitrate, sulfate, methane, and ferric iron among others. Either field or laboratory generated values for these parameters are acceptable.

Natural attenuation is accepted as the sole remedy when the following conditions have been met (WDNR, 1997d):

- Contaminant plume has been shown to be stable or receding
- Groundwater quality will be restored within a reasonable time frame
- All potential exposure pathways have been addressed
- There is no existing or anticipated threat to public health, safety or welfare or the environment during its implementation

Once this information is provided and an adequate monitoring program set in place, natural attenuation can be implemented. The site is then in monitoring and maintenance status governed by NRs 140 (WDNR, 1997a) and 724 (WDNR, 1997b). Any data collected during this time must support the conclusion that a plume is stable or decreasing, that contaminant mass is being reduced, that NR 140 groundwater standards (WDNR, 1997a) will be met in a reasonable time frame, and that potential receptors are not being impacted.

3.2.3 EUROPEAN ECONOMIC COMMUNITY

3.2.3.1 United Kingdom

Issues related to site remediation, groundwater protection, and the use of natural attenuation in the United Kingdom fall under the jurisdiction of the Environment Agency. The *Water Resources Act* (1991) (Environment Agency, 1991) places a duty on the

Environment Agency to monitor and protect water resources. *The Policy and Practice for the Protection of Groundwater* (Environment Agency, 1998) deals with waste disposal issues that may affect groundwater quality. Controlled substances fall into two categories (Environment Agency, 1998):

- List 1 substances are those considered most toxic. These substances must not enter the groundwater system.
- List 2 substances could be harmful if disposed of in large quantities.

The Environment Agency has developed and published the *Methodology for the Derivation of Remedial targets for Soil and Groundwater to Protect Water Resources* in October 1999 (Environment Agency, 1999). The methodology is based on a risk assessment approach incorporating a source-pathway-receptor analysis. The overall methodology is based on a tiered approach to determine risk based remedial targets. At each tier progressive data collection and analysis are required. A remedial target is derived for each tier but should be less onerous at each level due to additional processes (such as dilution or attenuation) that affect contaminant concentrations along its migration pathway to a receptor.

For groundwater, a Tier 1 evaluation considers whether contaminant concentrations in "pore water" in contaminated soil are sufficient to impact a receptor, ignoring dilution, dispersion, and attenuation along the pathway (Environment Agency, 1999). The "pore water" concentration can be actual measured values in soil or calculated concentrations based on partitioning equations. In a Tier 2 assessment, actual groundwater concentrations are compared to the target concentration. For Tier 3 and 4 evaluations, the groundwater concentration is compared to target concentrations multiplied by an attenuation factor. A receptor sensitivity analysis is also required as part of the initial site evaluation process. Target concentrations are ideally background levels. However, existing water quality standards, which are related to present or future groundwater use may also be used.

While no formal policy on use of natural attenuation currently exists, it has been accepted on a case-by-case basis at four sites in England and Wales (Smith, 1999). USEPA protocols and guidance are used by proponents and the Environment Agency for evaluating applications for natural attenuation. The National Groundwater and Contaminated Land Centre is currently developing a natural attenuation guidance document specific to the United Kingdom (Smith, 1999). It will be based on USEPA protocols and guidance but will be modified to address issues such as geology, hydrogeology and geochemistry that are relevant to the United Kingdom. For example, it will be modified to address groundwater flow in karst terrains and fractured crystalline bedrock (Smith, 1999).

3.2.3.2 The Netherlands

In the Netherlands, a decision support model has been developed to provide a stepwise approach for judging the potential for natural attenuation as a remediation strategy at a specific site (Sinke et al., 1998). The model covers both BTEX and chlorinated solvents. The decision model is depicted as a progressive route with four traffic lights (Sinke et al., 1998). Each traffic light represents a step in the evaluation of the potential for monitored natural attenuation as a remediation strategy at a site. An explanation of activities undertaken and information evaluated at each traffic light in the decision support model is provided in Table 3-6.

Table 3-6. **Information Evaluated at Each Traffic Light in the Netherlands Decision Support Model for Monitored Natural Attenuation (after Sinke, et al., 1998).**

TRAFFIC LIGHT	ACTIVITY
1	Analyze historical data Determine probability of monitored natural attenuation (MNA) Collect additional data in field or lab (if necessary)
2	Use a solute fate and transport model to calculate: • decrease in amount of contaminant with time • plume development and change in position
3	Discussion between regulator and proponent
	Determine acceptance of MNA
4	Implement MNA
	Develop long term monitoring program to:
	• evaluate the fate and transport model results and efficacy of MNA
	• protect receptors

At each light, the required information is evaluated and determined as good (green light), fair (orange light) or poor (red light). Fair ratings are indications that additional information must be collected. Poor ratings are an indication that natural attenuation is not appropriate for a given site.

The first two lights are based on technical and scientific information that can be used to evaluate existing data and whether natural attenuation is occurring, whether additional data must be collected, and to predict the long-term behavior of the contaminant plume. The apparent goal is to try and give an early indication of the potential for natural attenuation with as little expense as possible. At the third light, political and practical aspects, such as urban planning, future land use, and time frames are considered along with the previous data evaluation. The fourth light is the implementation of natural attenuation for a time period agreed upon by regulators and proponents. The model gives suggestions for a monitoring strategy. Monitoring focuses on verification of the analytical model used to predict the future behavior of the contaminant plume and on the ability of natural attenuation to protect receptors.

3.2.3.3 Denmark

The Danish Environmental Protection Agency (DEPA) has no formal policy on the use of natural attenuation as a remediation option (Dahlstrom, 1999). In keeping with a restoration principle contained in the Environmental Protection Act, they have issued Guidelines on Remediation of Contaminated Sites (DEPA, 1999). These guidelines provide a discussion of technical requirements for dealing with a contaminated site, from the investigation phase to the remedial phase. These guidelines cover contamination in soil, soil gas and groundwater from any source including industrial and commercial facilities as well as landfills.

Direction is also given on risk assessments. The assessments are carried out in three steps. Step three takes into account contaminant losses due to dispersion, sorption and degradation in both the saturated and unsaturated zones, when determining if a groundwater resource will be contaminated above the set groundwater criteria by a release.

3.3 DISCUSSION OF EXISTING LEGISLATION

Natural attenuation regulations do not vary significantly within U.S. Federal Departments or the ASTM, or from state to state in terms of lines of evidence required to prove natural attenuation or in characterization or monitoring required to obtain some form of site closure. Tables 3-7 and 3-8 provide a summary of selected information reviewed by each regulatory agency with a formal policy on natural attenuation. Where information is required by an agency on a particular natural attenuation component of policy, that

Table 3-7. Summary of Selected USEPA, ASTM, and DOD Information Reviewed During Evaluation of Natural Attenuation (NA).

NA COMPONENT	USEPA (USEPA, 1998, 1999)	ASTM (ASTM, 1998)	DOD (Wiedermeier et al., 1995)
Source Removal	x	x	x
Lines of Evidence			
- Historical Data	x	x	x
- Geochemical	x	x	x
- Microbial Data	x	Secondary Evidence	x
Site Characterization			
- Fate & Transport Modeling	x	x	x
- Source Delineation	x	x	x
- Groundwater Flow	x	x	x
- Phase Distribution	x	x	
- Extent of Contamination	x	x	x
- Receptors	x	x	x
Appropriate Site Description	x	x	x
Timeframe for Completion	ss	ss	ss
Monitoring			
- minimum number of wells	ss	ss	ss
- frequency	ss	ss	ss
- parameters	ss	ss	x
- duration	after objectives met[1]	uom[2]	uom[2]
Contingency Plan	x	x	x
Public Consultation	x	x	x
Offsite Migration	a	a	a

x – required ss – site specific [1] duration not specified uom – until objectives met [2] set by state a – allowed by policy

Table 3-8. Summary of Selected U.S. State Information Reviewed During Evaluation of Natural Attenuation (NA).

NA COMPONENT	Alaska	Florida	Michigan	Minnesota	Utah	New Hampshire	Texas	Wisconsin
Source Removal	x	x	x	x	x	x	x	x
Lines of Evidence								
- Historical Data	x	x	x	x	x	x	x	x
- Geochemical	x	x	x	x	x	x	x	x
- Microbial Data	x	x	x	nr	nr	x	nr	x
Site Characterization								
- Fate & Transport Modeling	x	x	x	x	x	x	x	x
- Source Delineation	x	x	x	x	x	x	x	x
- Groundwater Flow	x	x	x	x	x	x	x	x
- Phase Distribution	x	x	nr	nr	nr	x	nr	nr
- Extent of Contamination	x	x	x	x	x	x	x	x
- Receptors	x	x	x	x	x	x	x	x
Appropriate Site Description	x	x	x	x	x	x	x	x
Timeframe for Completion	ss	5 yrs[1]	ss	ss	ss	10 yrs[1]	ss	ss
Monitoring								
- minimum number of wells	ss	ss	6	ss	ss	ss	ss	ss
- frequency	ss	ss	quarterly	ss	quarterly	ss	ss	ss
- parameters	ss	ss	x	ss	ss	ss	x	x
- duration	uom	uom	uom	uom	uom	uom	uom	uom
Contingency Plan	x	x	x	x	x	x	x	x
Public Consultation	x	x	x	x	x	x	x	x
Offsite Migration	a	a	a	ns	a	ns	a	a

x – required nr – not required [1] may consider longer timeframe ss – site specificuom – until objectives met
a – allowed by state ns – not specified

information is denoted by an "x". In the cases of USEPA or DOD, line of evidence components are considered primary evidence whereas with the ASTM, microbiological data is only considered to be secondary evidence of natural attenuation potential. Natural attenuation components such as timeframe for completion or monitoring frequency or parameters are set by the governing state in most cases. However, states such as Florida, New Hampshire, Michigan and Utah have applied specific requirements for various components. Monitoring duration usually occurs until agency specified remediation objectives are met. The USEPA recommends monitoring after objectives have been met but does not specify a timeframe. Offsite migration is allowed by all agencies provided a proponent has agreement from adjacent landowners. In cases of offsite migration, all agencies recommend some form of institutional control such as a caveat on a land title.

The ASTM *Standard Guide for Natural Attenuation* (ASTM, 1998) provides a very good summary of the ASTM process for evaluating natural attenuation at a site. The USEPA MNA Directive (1999) and the ASTM RNA guide (ASTM, 1998) vary in that the ASTM guide is relevant only for petroleum hydrocarbons in groundwater. The USEPA Directive considers a much wider variety of contaminants of concern. Site characterization and remedy selection requirements are very similar.

All of the legislation reviewed have the following information requirements in common:

- Lines of Evidence
- Source Removal
- Site characterization
- Modeling
- Monitoring
- Performance evaluation
- Contingency measure development

These and other information requirements are discussed below.

3.3.1 LINES OF EVIDENCE

Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites (USEPA Directive, USEPA, 1999), discusses three lines of evidence that are required to evaluate efficacy of MNA at a site. The site investigation must provide enough information to satisfy those lines of evidence. Fate and transport modeling can also be used to evaluate data and make predictions on plume behavior and timeframe for completion of a remediation program.

The USEPA *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (USEPA Protocol, USEPA, 1998) also requires evaluation of lines of evidence. However, the USEPA Protocol has been expanded to include additional geochemical data for processes involved with chlorinated solvents such as reductive dechlorination.

There are a few differences between the lines of evidence required by the ASTM Guide (1998) and the USEPA Directive (USEPA, 1999). The USEPA Directive requires primary and secondary lines of evidence to support MNA while the ASTM Guide indicates that primary evidence is sufficient. The USEPA Directive requires tertiary evidence when primary and secondary evidence is inadequate or inconclusive. Secondary evidence is required by the ASTM Guide when no historic information is available for a site. The ASTM Guide considers RNA for plumes that are increasing in size if risk reduction and performance goals are met whereas the USEPA Directive favours implementation of MNA at sites with shrinking plumes or plumes that are no longer increasing in size.

All of the states reviewed require some form of fate and transport modeling as part of submission of a proponent's application to the regulator for permission to use natural attenuation as a site remedy. Most states do not specify a particular modeling program to be used. MDEQ (State of Michigan) is apparently the only agency that allows tracer studies to be used in one of its required lines of evidence as proof of natural attenuation (MDEQ, 1998b).

3.3.2 SOURCE REMOVAL

The USEPA Directive (USEPA, 1999) is written with the expectation that source removal or control will be evaluated and implemented for all sites. However, it does not discuss whether monitored natural attenuation can be used for source control. The ASTM Guide (ASTM, 1998) also favours source removal for all RNA sites.

All legislation support the concept of source control whether through source removal or containment. This aspect of site remediation is seen as critical to success of natural attenuation at a site. Texas has recently undertaken a study of all plumes associated with underground storage tanks (Mace et al., 1997). Average plume lengths for sites with, and without, source removal were compared. The study indicated that no significant difference existed in length of the plumes. Therefore, source control was not always deemed necessary.

Pardieck and Guarnaccia (1999) argue that source zone attenuation could be defined as the reduction of the mass flux of contaminants to groundwater by naturally occurring processes and that natural attenuation is a viable means of controlling the contaminant source. In other words, natural attenuation results in a reduction in mass transfer from source to the plume rather than a percent or total loss of source mass. Based on this definition, monitored natural attenuation may be appropriate for stable or shrinking groundwater plumes particularly in cases where a contamination event occurred many years ago.

3.3.3 SITE CHARACTERIZATION

In discussing implementation of natural attenuation at a site, the USEPA Directive (USEPA, 1999) stresses a need for adequate site characterization to demonstrate efficacy of natural attenuation processes. The level of site characterization is considered to be more thorough than for other active remediation methods. Site characterization for natural attenuation requires a quantitative understanding of source mass; groundwater flow (including preferential pathways), contaminant phase distribution and partitioning between soil, groundwater and soil gas; rates of biological and non-biological transformations; and an understanding of how all these factors are likely to vary with time (USEPA, 1999). The USEPA Directive also advocates use of a conceptual site model for integrating data and guiding investigative and remedial actions. Site characterization must also be adequate to determine real and potential affects to receptors.

Data collection requirements in the USEPA Protocol (USEPA, 1998) for site characterization have also been expanded to account for different contaminants and natural attenuation processes. Information must also be collected on degradation by-products and intermediates. This information is generally not required for fuel hydrocarbon sites.

DOD requirements (Wiedermeier et al., 1995) are not really a policy, but rather a comprehensive "how to" manual designed originally for Air Force personnel. It is presented more from the proponent's perspective than the regulator's perspective and practical in nature. For example, it provides very good explanations of all aspects of site and contaminant characterization rather than a discussion of regulatory requirements for completing an application for approval by the regulator for use of natural attenuation as a site remedy. The DOD Protocol (Wiedermeier et al., 1995) discusses lines of evidence that can be used to support use of intrinsic remediation at a site. Discussion of evidence is geared mainly towards biodegradation of fuel hydrocarbons. The DOD Protocol provides a clear discussion of requirements for site characterization and evaluation of potential biodegradation processes. However, it lacks guidance on the affects of different soil types on site characterization or how climatic conditions (e.g. temperature or a shorter warm season) may affect assessment of biodegradation processes. The site characterization component emphasizes development of a model for evaluating fate and transport of contaminants rather than a comprehensive understanding of the site. Consequently, data requirements are potentially those of the model rather than those of the regulator. Explanations of the different biodegradation processes are provided which gives an aid to understanding why data are collected.

Site characterization is viewed by each U.S. state agency as a key factor in understanding the potential for natural attenuation at a site. Each of the states' natural attenuation protocols require information for determining a site's geology and hydrogeology as well as fate and transport of contaminants of concern. Florida, (FDEP, 1998), New Hampshire (NHDES, 1998), and Wisconsin (WDNR, 1997d) provide the greatest detail for site characterization requirements. Florida divides site characterization into three levels of evaluation that build on each other with reporting and review checks to ensure that a proponent does not put in unnecessary effort into a site that is not suited to natural attenuation. The most detailed protocols, such as those of Wisconsin (WDNR, 1997d), provide actual lists of parameters and acceptable analytical methods for geochemical and contaminant characterization portions of site characterizations.

3.3.4 DESCRIPTION OF APPROPRIATE SITES

Most protocols provide a discussion on sites where natural attenuation may be appropriate and where natural attenuation should not be applied. This is useful in that proponents understand up front whether natural attenuation will be considered by regulators for a particular site. Favourable sites are those where natural attenuation is protective of human health and the environment, where the plume is stable or shrinking, where environmental conditions are not likely to change over time, and where drinking water supplies or other receptors will not be adversely affected if natural attenuation is chosen as a remediation option.

3.3.5 TIMEFRAME FOR COMPLETION

Another concept common to all MNA protocols is the need for natural attenuation remedy to deal with site contamination in a reasonable amount of time. The majority of protocols simply call for a comparison between MNA and other remediation alternatives. The timeframe for natural attenuation must be comparable to that of a viable active remediation method. New Hampshire (NHDES, 1998) specifies a time period of ten years as the maximum required time for MNA to meet remediation objectives. Florida (FDEP, 1998) recommends a timeframe of five years for natural attenuation to meet remediation objectives. However, both protocols do allow adjustments to the timeframe on a site-specific basis.

3.3.6 POST-IMPLEMENTATION MONITORING

Post implementation long-term monitoring forms a critical component of the use of natural attenuation at a site. The USEPA Protocol (USEPA, 1998) for chlorinated solvents indicates that two types of monitoring are required: performance monitoring and compliance monitoring. Performance monitoring wells are located upgradient of a plume, within the plume, and adjacent to the downgradient edge of the plume. These wells are used to verify predicted performance of natural attenuation processes and mechanisms evaluated for the site. Compliance monitoring is used to ensure that potential receptors are not affected by contaminants at the site. The USEPA Protocol discusses two types of compliance wells: point of action and sentry wells. Point of action wells are located at points past which expansion or migration of a plume will not be allowed. These wells trigger implementation of contingency plans for a site. Sentry wells are located between the furthest downgradient performance monitoring well and point of action wells. They can be used to provide early detection of plume migration.

The final configuration of both performance and compliance wells is dependent on site and contaminant characteristics. Factors such as groundwater velocity and distance to receptors are to be taken into account. Analytical protocols will be mainly influenced by contaminant type. Sampling frequency is determined by plume behavior, contaminant travel times, distance between the various performance and compliance wells, and distance to receptors. There appears to be a trend towards quarterly monitoring, with potentially reduced monitoring frequency over time.

The DOD long-term monitoring protocol (Wiedermeier et al., 1995) does not specify a time frame or sampling frequency. Instead, the number of wells, sampling frequency, and duration of monitoring are left as site-specific items to be discussed with the local regulator. This is because regulations can and do vary across the United States and the protocol is meant to be used for any site in any part of the country.

Both the USEPA Directive (1999) and the ASTM Guide (ASTM, 1998) recognize that the length of performance monitoring is site specific, but the USEPA Directive specifies that monitoring should continue one to three years after remediation objectives have been met.

Post implementation monitoring is a critical area discussed by each of the state protocols. Guidance documents specify monitoring periods and program requirements both in terms of parameters and duration. States such as Wisconsin (WDNR, 1997d) and New Hampshire (NHDES, 1998) require monitoring until specific soil and groundwater criteria are met. Florida (FDEP, 1998) requires comparison of monitoring results with annual milestone reductions in concentrations. In addition, proponents must re-evaluate model predictions and natural attenuation effectiveness based on trends in the data. Utah (UDEQ, 1999) specifies the monitoring duration on a case-by-case basis.

3.3.7 CONTINGENCY PLAN

All MNA protocols recognize the need for contingency measures in the event MNA or RNA does not meet remediation objectives. Contingency plans must specify exact actions to be taken should the plume not behave as expected. New Hampshire (NHDES, 1998) specifically requires a financial bond for all remediation programs. The financial bond ensures a proponent will maintain interest a site and that funds are available to the regulator should a proponent fail to meet remediation obligations or objectives.

3.3.8 PUBLIC CONSULTATION

All state MNA protocols indicate that public participation should be considered when developing any remediation program particularly in the case of groundwater contamination. However, while most states indicate that public notification should be done, very few of the states indicate that public consultation is a requirement even in the case of offsite contamination. New Hampshire (NHDES, 1998) considers the contaminant plume to be a groundwater management zone regardless of its extent. Proponents are required to notify all owners of lots within the zone within 30 days of regulator approval.

3.3.9 OFFSITE MIGRATION

All state agencies, with the exception of Minnesota and New Hampshire, allow for contamination that extends beyond the property boundary. Minnesota's (MPCA, 1998b) and New Hampshire's (NHDES, 1998) regulations do not explicitly indicate that offsite migration is allowed. Regardless, legislation requires that receptors are identified and that a plume does not extend into groundwater management zones. Point of compliance wells are required and monitoring is required to ensure that remediation objectives are not exceeded.

3.3.10 OTHER LEGISLATION COMPONENTS

The USEPA Protocol (USEPA, 1998) uses a scoring system during initial bioattenuation screening process. Once geochemical data for a site have been collected, the site is scored based on a comparison of the analytical result for a parameter with a table of desired analytical results contained in the protocol. Depending on the total score for the site, a proponent may or may not proceed to other steps in the screening process. The scoring mechanism is useful for providing regulators and proponents with some means of determining whether to consider monitored natural attenuation as the correct approach to site remediation. However, such a protocol and scoring system can be abused and used in a cookbook fashion where total points are stressed over a thorough evaluation of data provided in support of natural attenuation. Proponents may tend to score a site favourably using incomplete or inadequate data. Regulators can assist proponents by making information requirements clearly understood. Regulators may err by simply looking for a parameter in the proponent's submission and awarding points without fully understanding how all natural attenuation processes fit together in a remediation program and how the data relate to those processes. Therefore, it is important that regulators responsible for review of natural attenuation remedies are adequately trained in the scientific aspects of MNA.

Norris and Wilson (1999) provide a discussion on their experiences with using the USEPA chlorinated solvents protocol (USEPA, 1998) and potential problems with it's scoring system. They indicate that, at some sites, there are insufficient solvent concentrations to yield chlorine values, upon reductive dechlorination, above background values. Even though the data showed clear evidence that reductive dechlorination was taking place, a lower score would be given in that instance than if chloride values in the plume were above background levels. Conversely, in the case of landfill leachate plumes, chlorides in leachate may be an order of magnitude higher than chlorides produced by reductive dechlorination. There would be no way to distinguish between these chlorides. A high score could be given for the leachate chlorides without any proof that reductive dechlorination was occurring at a site.

Problems can also occur with dissolved oxygen readings depending on the analytical method or geology of a site. Care must be taken not to create air bubbles when using the Winkler method for dissolved oxygen. This can result in an elevated dissolved oxygen reading and a lower score than appropriate for the site. Very slow purge rates in tight soils such as clay or till must be used to avoid introduction of air into a well or the gravel pack around the well screen. This could result in an elevated dissolved oxygen reading (and thus a lower score) that is not typical of, or appropriate for, an aquifer. Based on the scoring examples provided in the USEPA Protocol, points are subtracted for dissolved oxygen readings above 0.5 mg/L even though the USEPA Protocol indicates that points should not be subtracted until dissolved oxygen readings are above 5 mg/L. Thus, sites with dissolved oxygen levels in a contaminant plume slightly above desired levels are penalized even though other evidence may indicate that bioattenuation is occurring.

The scoring system also awards points according to the number of degradation intermediates identified by monitoring. The more intermediates found, the more points awarded. Therefore, a site where perchloroethene and 1,1,1-trichloroethane are released (with seven resulting intermediates observed) would be given a higher score than a site with iron-reducing or aerobic conditions downgradient where trichloroethene was released and the only potential intermediate (cis-dichloroethene) was observed. Norris and Wilson (1999) argue that the direct evidence provided by intermediates should not be more important than indirect evidence provided by geochemical data. They suggest that the best evidence for or against natural attenuation is five or more years of quarterly monitoring results. Given their discussion, it is apparent that careful interpretation of data is warranted to determine if points are being properly awarded. It is also apparent that natural attenuation can be an appropriate remediation option at a low scoring site should sufficient support be provided by indirect geochemical evidence or evidence for control by non-destructive attenuation mechanisms.

Minnesota also uses a scoring system in the screening portion of the site evaluation. However, in Minnesota, the scoring system is used to determine at the outset if natural attenuation should be pursued rather than as one component of the site screening. The information reviewed and the associated scores are very similar to the USEPA Protocol and have the same potential problems.

The DOD Protocol (Wiedermeier et al., 1995) is contained in two volumes. The first volume contains guidance on natural attenuation processes and mechanisms and appendices that provide information on data collection techniques. These appendices provide a lot of detailed information for site evaluation such as site characterization including well installation techniques and soil and groundwater sampling methods. Therefore, the DOD Protocol is a very good general reference for these items. There is a good section on sample handling and QA/QC requirements that makes a user aware of the importance of collecting good representative samples. The appendices also contain a "how to" guide for the preparation of site investigation reports. Examples are provided for constructing cross sections, flow nets, and other maps and diagrams. Sample calculations are also provided for aquifer parameters such as flow velocity and for hydraulic conductivity based on well test data. Sample calculations are provided for contaminant behavior processes such as partitioning. This section is very useful for users wishing to understand the calculations and to prepare their own reports rather than relying solely on outside consultants. The second volume of the DOD Protocol contains two case studies. These case studies provide further examples of site characterization, and aquifer and degradation calculations, and allow a user to see how all the information comes together in evaluating intrinsic remediation at a site.

The ASTM Guide (ASTM, 1998) indicates that remediation goals are determined by application of site-specific risk based corrective action. Goals may be site-specific target concentrations or performance criteria including containment. States with explicit policy and guidance on MNA list remediation objectives related to soil and groundwater. Any proposal for MNA must demonstrate that those objectives can be met. All states reviewed allow for development of site-specific objectives based on land use or background quality conditions as an alternative to meeting proscribed objectives. Development of alternative objectives seems to be allowed only in instances where background conditions are proven to exceed proscribed objectives or where receptor risk has been adequately characterized. An interesting feature of the New Hampshire Rule Env-Wm 410 (NHDES, 1993) is that it builds in changes to criteria for some compounds based on changes to detection limits. If the detection limit, for example for benzo(a)anthracene, becomes less than the current ambient criteria, the lower detection limit then becomes the new ambient criteria.

Economic feasibility must also be evaluated when reviewing the applicability of natural attenuation at a site. The costs associated with natural attenuation must be evaluated against those of other potentially effective remediation options.

Each agency has a clearly defined process for a proponent to apply for permission to use MNA at a site and an approval process that must be followed before MNA can be implemented. New Hampshire charges a fee for implementation of any remedial action at a site (NHDES, 1993).

A key aspect of all the legislation is the identification and protection of potential receptors. Michigan's site classification (MDEQ, 1996) is based on three levels of risk to receptors. Based on the classification, only active remediation solutions such as pump and treat or vapour extraction systems would be considered. Receptors in the Michigan Protocol include water wells, buildings, ecosystems, and aquifers. Receptors must be identified and pathway or pathways to receptor properly characterized. Natural attenuation will only be considered if it is proven that receptors are adequately protected from harm. Institutional controls such as deed restrictions, restrictive covenants or wellhead protection agreements could be used as a means of ensuring protection of receptors.

Several states such as Wisconsin (WDNR, 1997d), Florida (1998b), Utah (UDEQ, 1999) and New Hampshire (NHDES, 1998) provide very good guidance on site characterization and other informational requirements for natural attenuation. These protocols not only provide a list of information required for an application but also a discussion of each item and its relevance to various natural attenuation processes. Minnesota (MPCA, 1997) also provides an excellent screening checklist for applications for natural attenuation as well as sample calculations for biodegradation rate studies. Utah's guidelines for corrective action (UDEQ, 1999) are comprehensive, guiding a proponent through a series of steps and listing information required at each step that must be addressed before they are allowed to move to the next step. An extensive section on calculations is included as is a checklist for site information requirements.

Canadian approaches reviewed do not provide any background to natural attenuation processes or information required to determine whether natural attenuation is appropriate at a site. Ontario's Procedure B-7-1 (MOEE, 1994a) mentions a contaminant attenuation zone but provides no guidance as to what information is required to characterize this zone. Alberta's Management Framework for Oil and Gas Lease Sites (AENV, 1999a) also mentions natural attenuation but only in the form of a definition. British Columbia's regulations (BC 1996, 1999) do not mention natural attenuation at all as a specific remediation option. Consequently, none of these documents are particularly useful for the development of natural attenuation protocols or guidances.

The most complete guide reviewed for Europe regarding use of natural attenuation is the traffic light system developed by the Netherlands (Sinke et al., 1998). It provides a decision mechanism for evaluating applicability of natural attenuation but does not provide detail on what information is required by the regulator. The United Kingdom is currently developing a natural attenuation document that will be an adaptation of the USEPA protocols (Smith, 1999).

4.0 CASE STUDIES

There has been considerable documentation of natural attenuation successfully applied to sites in the United States. However, little documentation is available for sites in Canada. If a policy on natural attenuation is to be developed for Alberta it must be demonstrated to work with physical and climatic conditions found in Alberta. To that end, three sites in

Alberta with an implied potential for natural attenuation were reviewed. The natural gas processing plant and the petrochemical facility were chosen due to the range of potential contaminants involved and the availability of site monitoring data. The refueling facility was chosen due to its northerly location and to examine the potential affects of colder temperatures on natural attenuation processes.

The potential for considering natural attenuation in a regulatory framework in Alberta was examined based on screening of data provided and against existing protocols and guidance documents published in the United States. This screening was done to determine whether the data available met information required by other jurisdictions and if so, whether the potential for natural attenuation was supported by that information.

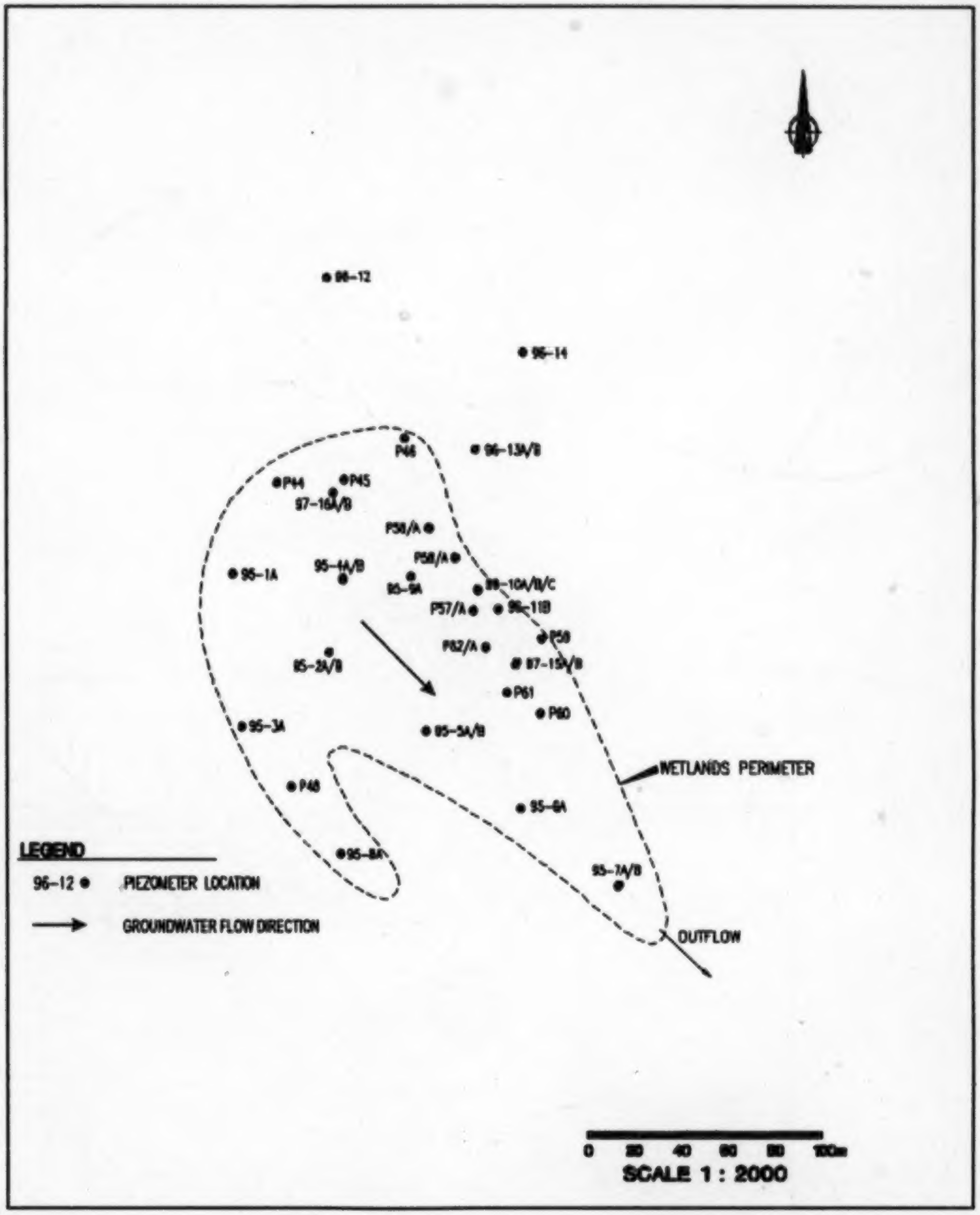
4.1 ALBERTA CASE STUDIES

4.1.1 SITE A – NATURAL GAS PROCESSING PLANT, WEST-CENTRAL ALBERTA.

In 1996, a study was initiated to evaluate natural attenuation of common oil industry contaminants in wetlands (Komex, 1999). One of those wetlands is situated adjacent to a natural gas processing plant in west central Alberta. Free phase and dissolved phase condensate has been observed discharging to the wetland since at least 1984. The condensate enters the wetland via groundwater transport at approximately one metre below ground surface. The lateral extent of the contamination in the wetland has not increased since the surface extent of the plume was delineated in 1986. Since monitoring began, the outflow has remained free of hydrocarbons. Contaminant transport calculations incorporating retardation due to sorption indicate that the plume should have moved approximately 40 metres since being delineated in 1986. Therefore, other natural attenuation mechanisms other than sorption were suspected to be taking place.

Piezometer locations within and adjacent to the contaminated area are shown in Figure 4-1. Dissolved oxygen measurements (typically < 0.1 mg/L) indicate that the

Figure 4-1. Piezometer Locations and Direction of Groundwater Flow at a Natural Gas Processing Plant in West-Central Alberta (after Komex, 1999).



96-12
96-14
P46
96-13A/B
P44
P45
97-16A/B
P50/A
P58/A
95-1A
95-4A/B
95-9A
99-10A/B/C
P57/A
96-11B
P59
P62/A
95-2A/B
97-15A/B
P61
P60
95-3A
95-5A/B
WETLANDS PERIMETER
P48
95-6A
95-8A
95-7A/B
OUTFLOW
LEGEND
96-12 ●
PIEZOMETER LOCATION
GROUNDWATER FLOW DIRECTION
0
20
40
60
80
100m
SCALE 1 : 2000

contaminated groundwater is anaerobic prior to entering the wetlands. Within the saturated zone of the wetland (both contaminated and background locations), conditions are generally anaerobic, indicating that oxygen consumption is equal to or greater than the rate of oxygen diffusion from atmosphere and rainfall. Any potential biodegradation occurring in the wetland would be occurring under anaerobic conditions.
The objectives of the 1996 study were (Komex, 1999):

- Characterize and delineate contaminant distribution in the wetland
- Evaluate occurrence of natural attenuation and identify evidence for individual attenuation mechanisms
- Conduct laboratory testing to evaluate factors controlling biodegradation and sorption onto the peat

The study established the following:

- Groundwater flow occurs in three zones: the near surface peat, the lower peat, and the underlying clayey silt till, with flows varying due to seasonal changes
- Wetland outflow was free of contaminants
- Peat was three times more sorptive than clayey silt till
- Geochemical evidence supported iron (III), manganese (IV), and sulphate reduction
- Peat's limited carbon content makes it a poor substrate for microorganisms suggesting that hydrocarbons entering the wetland could alternately be used as a substrate for microbiological consumption
- Nitrogen and phosphorus are present in sufficient quantities to enable biodegradation

Additional study was undertaken in 1997 (Komex, 1999) to monitor for direct evidence of natural attenuation, to monitor the natural attenuation processes identified, to evaluate aquatic toxicity, and to assess the importance of biodegradation, volatilization, and sorption.

Results of the study indicated the following (Komex, 1999):

- Analytical data from historical sampling provided evidence of a shrinking hydrocarbon plume
- Anaerobic biodegradation by iron, manganese, and sulphate reduction was confirmed by geochemical data and microbiological enumeration
- Volatilization was observed and a rate estimated at 0.1 kg/day
- Aquatic toxicity tests indicated significant toxicity at inflow locations and no evidence of toxicity at outflow locations
- Aerobic biodegradation was observed in the unsaturated zone

Occurrence of near surface aerobic biodegradation was evaluated by sampling O_2 and CO_2 concentrations collected in vapour collection vessels installed at surface and by vapour probes installed at 0.5 metres below ground surface. The data collected for the site were used to calculate rates of O_2 consumption and CO_2 production (Table 4-1) that would indicate biodegradation was occurring and allow for calculation of a biodegradation rate. Based on the oxygen consumption rates, an average degradation rate of 27 mg hydrocarbon per kilogram of soil per day was calculated.

Table 4-1. Average O_2 Consumption and CO_2 Production Rates in Vapour Collection Vessels Installed Near a Wetland in West-Central Alberta.

DATE	Average O_2 Consumption Rate (percent O_2 consumed/3 hrs).	Average CO_2 Production Rate (percent O_2 consumed /3 hrs).
July 29, 1998	0.68	0.8
August 6, 1998	1.4	2.2
August 13, 1998	1.3	2.2
September 11, 1998	1.4	1.8

To provide indirect evidence of contaminant degradation, dissolved oxygen, dissolved iron, sulphate and manganese levels were monitored in groundwater at the site. Distribution of iron, manganese, sulphate, and BTEX levels across the site are shown in

Figure 4-2. Dissolved oxygen levels within the plume were lower than levels outside the plume (typically <1.1 mg/L versus 2 to 3 mg/L). Dissolved iron and manganese levels were elevated within the plume area and sulphate levels were reduced. This suggests that biodegradation via iron, manganese, and sulphate reduction was occurring.

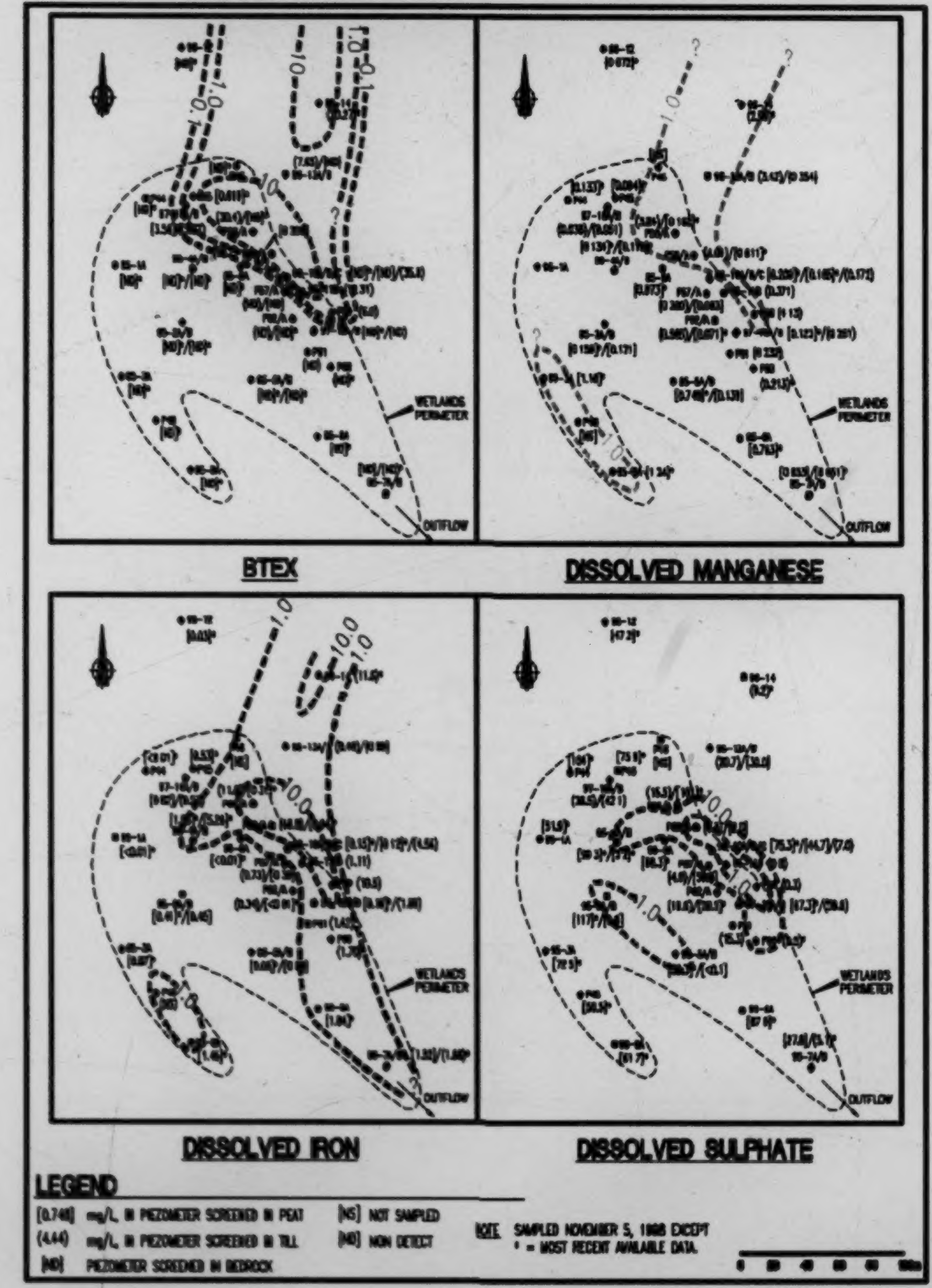
4.1.2 SITE B - PETROCHEMICAL FACILITY, EAST-CENTRAL ALBERTA.

A company operates two ethylene units and one polyethylene unit on their site. In 1994, the company proposed a groundwater management plan based on risk assessment of the site (Stehmeier, 1999). A probabilistic risk analysis model suggested groundwater contamination would be remediated before reaching bedrock and surface water receptors. Remediation, according to the model, involved intrinsic biological degradation. A compliance well network was installed to monitor site groundwater and validate the risk analysis model.

The surficial deposits at the site are mainly of glacial origin (Stehmeier, 1999). A glacial till blanket has been deposited directly over bedrock, with only occasional minor sand accumulations reported between the till and bedrock formation at the site. The till deposits range from three to 18 metres in depth with the most common thickness being six to 11 metres. The deposits consist of two till sheets: upper ablation till (till composed of drift in transport on a shrinking glacier) and lower till. Commonly the upper till is characterized by a brown and rusty color while the lower till is gray in color. Sand lenses are present between the till sheets and overlying the bedrock at the base of the till. Site data suggested these sand lenses are generally thin and laterally discontinuous (Stehmeier, 1999). The wells for this site are located in the upper till.

A buried valley lies to the south of the site where the bedrock elevation drops abruptly. This valley results in a dramatic increase in the thickness of the basal till but the upper till remains fairly uniform. Bedrock consists of shale to a depth of approximately 30 metres with two sandstone layers (representing a thickness of 3.6 to 4 metres) found in the next

Figure 4-2. Distribution of BTEX and Geochemical Indicators of Biodegradation in a Groundwater Plume at a Ntural Gas Processing Plant in West-Central Alberta (after Komex, 1999).



BTEX

DISSOLVED MANGANESE

DISSOLVED IRON

DISSOLVED SULPHATE

WETLANDS PERIMETER
OUTFLOW
1.0
0.1
10.0
?
LEGEND
[0.748] mg/L, IN PIEZOMETER SCREENED IN PEAT
(4.44) mg/L, IN PIEZOMETER SCREENED IN TILL
[ND] PIEZOMETER SCREENED IN BEDROCK
[NS] NOT SAMPLED
[ND] NON DETECT
NOTE SAMPLED NOVEMBER 5, 1998 EXCEPT
* = MOST RECENT AVAILABLE DATA.
0 20 40 60 80 100m

nine metres (designated as Sandstone #1). Below this more shale is found to a depth of approximately 67 metres where a massive sandstone unit (Sandstone #2) exists more than 30 metres thick. A shale and sandy shale unit underlie this sandstone.

Hydraulic conductivities range from 1×10^{-4} to 4×10^{-7} cm/s in the upper till, 1×10^{-6} to 9×10^{-8} cm/s in the basal till, and 2×10^{-2} to 1×10^{-4} cm/s in sand lenses within the tills. Hydraulic conductivity in the underlying bedrock (shale) ranges from 2×10^{-4} to 7×10^{-7} cm/s with the sandstone aquifers ranging from 1×10^{-3} to 3×10^{-3} cm/s. Groundwater movement vertically through the till formation is expected to be slow. Horizontal groundwater migration is expected to take place mainly across the zones of higher hydraulic conductivity.

Two main aquifers exist below the plantsite. The lower aquifer (Sandstone #2) is confined. The upper aquifer (Sandstone #1) is unconfined. The hydraulic vertical gradient is directed downward with a strong recharge trend. Groundwater in the glacial drift and till/bedrock interface also stabilized at elevations above the piezometric levels of both bedrock aquifers, suggesting a recharge condition on the plantsite.

In 1998, groundwater monitoring at the site indicated nine monitoring wells were impacted by organic chemicals (Stehmeier, 1999). Figure 4-3 shows locations of monitoring wells within the effected plant site production area. Figures 4-4 and 4-5 show changes in benzene and terminal electron acceptor (TEA) concentrations with time. One well, GW-440-8B-SL, showed an upward trend for benzene between 1994 and 1998. This well is located near a known area of impact (historical surface spills and sump overflows of C5+ product). Contamination sources (surface spills and sump overflows) have been under control since 1996 (Stehmeier, 1999). Specifically, the case study site is located between a fire line trench and a storm sewer trench which are assumed to act as major hydraulic sinks in the area.

Contamination at this site consists of C5+ components. C5+ is a mixed hydrocarbon consisting of primarily benzene. Other components of significance are dicyclopentadiene,

Figure 4-3. Monitoring Well Locations at a Spill Site Within a Petrochemical Facility in East-Central Alberta (after Stehmeier, 1999).

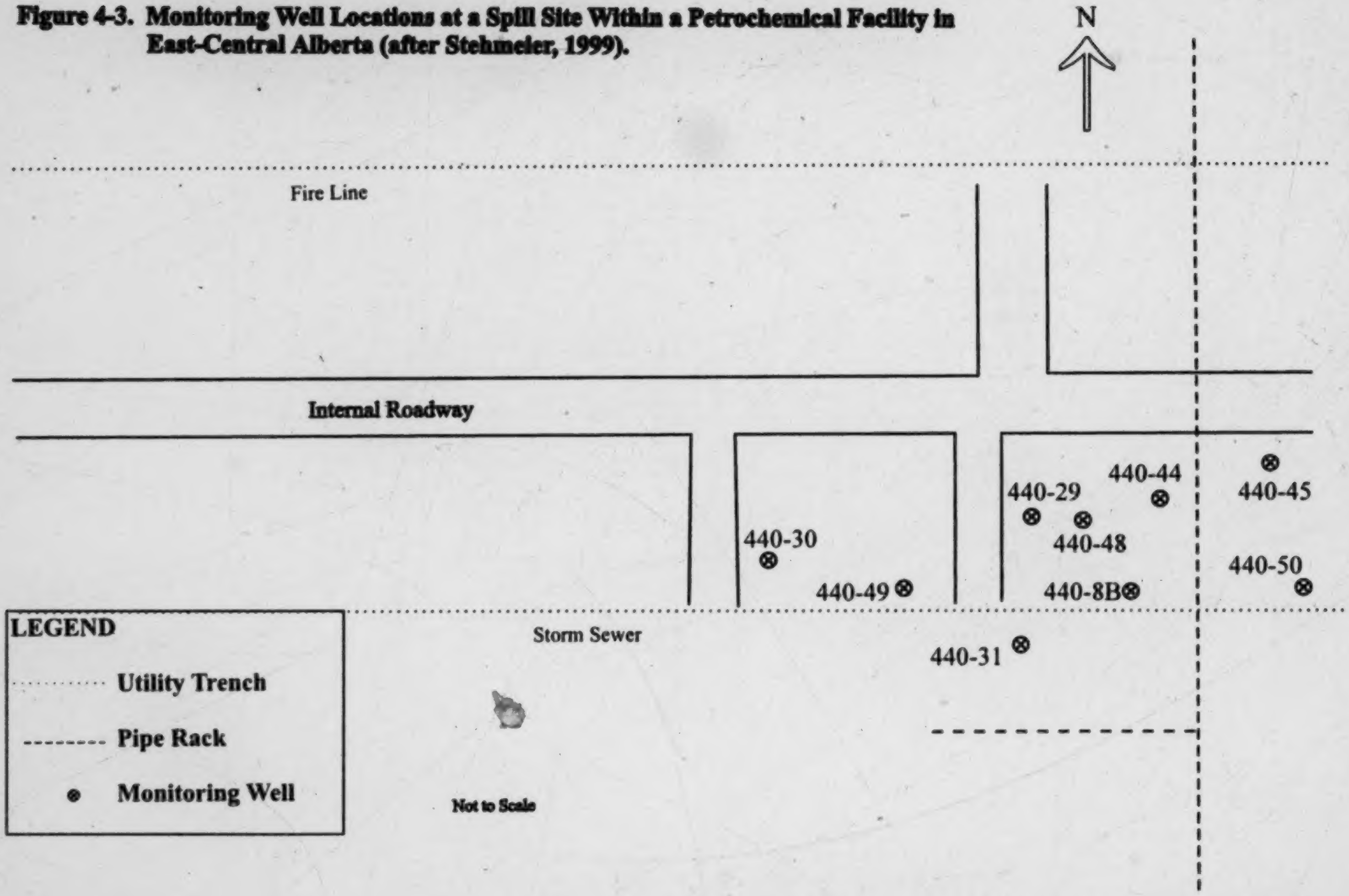

N
Fire Line
Internal Roadway
Storm Sewer
440-29
440-44
440-45
440-48
440-30
440-50
440-49
440-8B
440-31
LEGEND
Utility Trench
Pipe Rack
Monitoring Well
Not to Scale

Figure 4-4. Monitoring Well 440-8B-SL - Changes in Benzene and Sulphate Concentrations with Time at a Spill Site Within a Petrochemical Facility in East-Central Alberta (after Stehmeier, 1999).

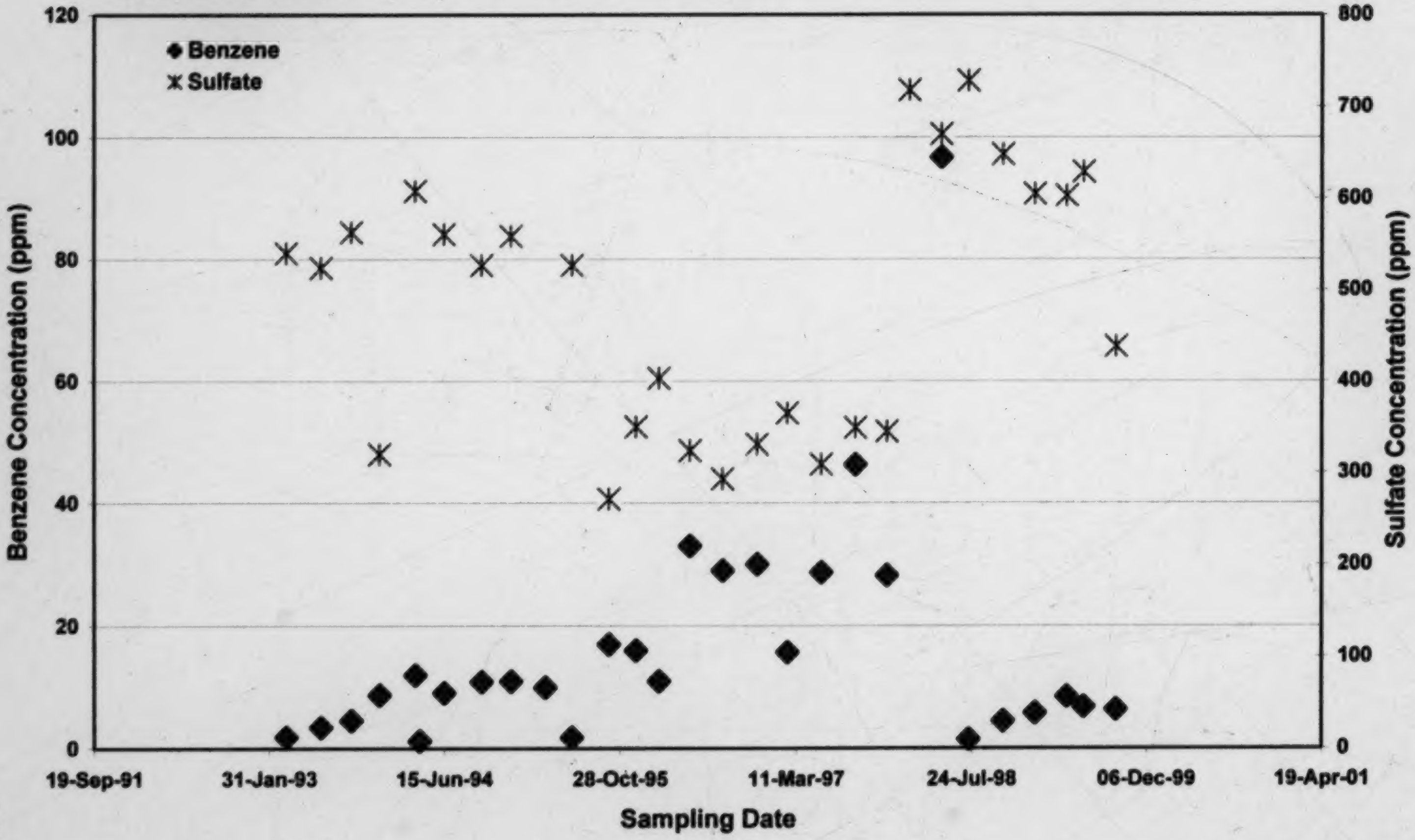
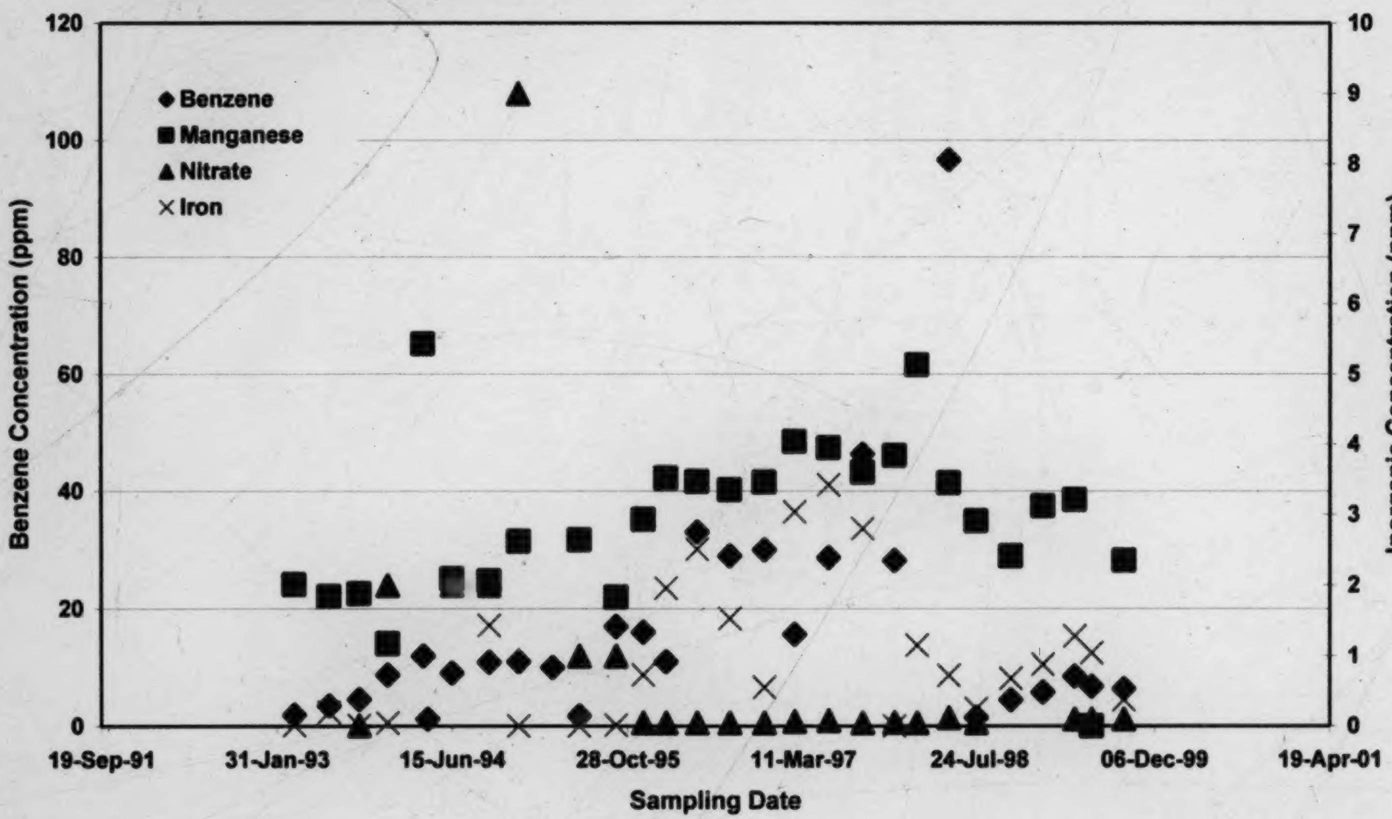


Figure 4-5. Monitoring Well 440-8B-SL - Changes in Benzene, Manganese, Iron (II), and Nitrate Concentrations with Time at a Spill Site Within a Petrochemical Facility in East-Central Alberta (after Stehmeier, 1999).



cyclopentadiene, toluene, styrene, pentene-1, cyclopentene, isoprene, naphthalene, 1,3-butadiene and indene. Other components with greater than 1% of the hydrocarbon content are C10, C6, C5 and C9 mixtures.

GW-440-8B-SL (Figures, 4-4, 4-5) has been monitored quarterly for routine groundwater quality parameters, organics, metals, and nutrients since 1993. Other wells in proximity have been monitored less regularly also since 1993 for benzene, toluene, ethylbenzene, dicyclopentadiene, nitrate, iron, manganese, and sulphate.

As part of a project using stable isotopes for measuring in situ bioremediation, microbiological counts were made using most probable number techniques in a minimal salts medium with C5+ as the carbon source. Based on the data for this site the proponent concluded that (Stehmeier, 1999):

- Soluble manganese (Mn^{+2}) increased with benzene concentration, as did ferrous iron (Fe^{+2})
- Nitrate decreased to minimum levels as benzene concentrations increased
- Sulfate concentration was high but decreased as benzene concentration increased and then sulfate increased again as benzene concentration decreased

All these patterns were considered by the proponent to be consistent with a site undergoing active biodegradation where the electron acceptors were Mn^{+4}, Fe^{+3}, SO_4^{-2}, and NO_3^-.

4.1.3 SITE C - PETROLEUM, LUBRICANT AND OIL TANK FARM AT A REFUELING FACILITY, NORTHEASTERN ALBERTA.

This site has had a number of recorded spill events that have contributed to the contamination present at the site. In May 1989, 20,000 litres of aviation fuel were spilled (Biggar, 1998). The spill was vacuum recovered but 2,300 litres were not accounted for.

In 1995, three spills totaling approximately 14,000 litres occurred (Biggar, 1998). Approximately 6,200 litres were not recovered.

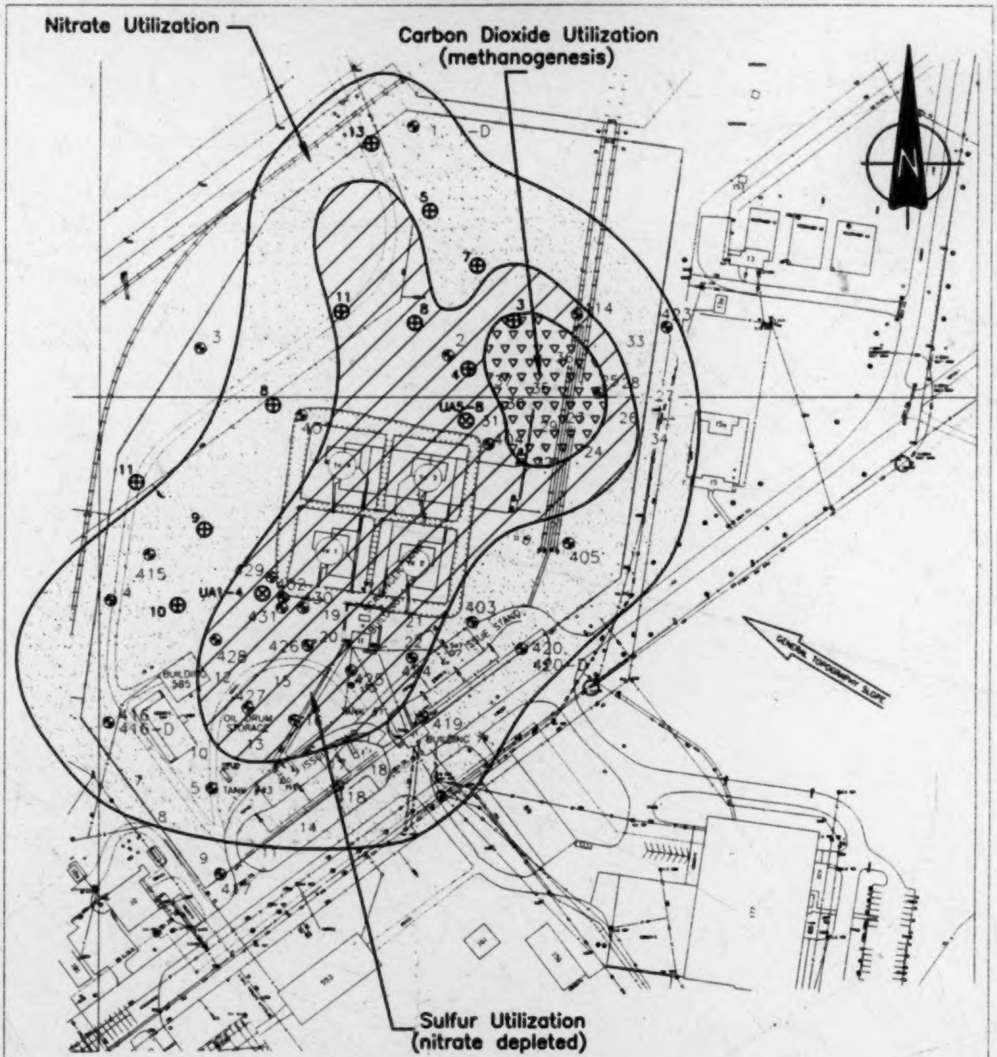
Since 1993, a number of studies have been undertaken to determine the degree and extent of contamination as a result of spillage in the tank farm (Biggar, 1998). Studies were conducted in 1993, 1995 and most recently in the spring and summer of 1997. The latest investigations were conducted to assess the potential for intrinsic bioremediation of the fuel spillage and to determine the potential for offsite migration to sensitive receptors. A total of eight new wells were installed in 1997. The wells were installed as nests of four wells at two locations. Soil and groundwater samples were collected from each location. Groundwater was also sampled at 15 additional locations using a drive point sampler. Groundwater monitoring wells from previous studies were also sampled as part of the 1997 investigations (Biggar, 1998). Sample locations are shown in Figure 4-6.

Groundwater samples were analyzed for hydrocarbons (BTEX, total purgeables and total extractables), terminal electron acceptors (dissolved oxygen, nitrate, nitrite, sulphate), biodegradation byproducts (methane, soluble iron), pH, redox potential, conductivity, and temperature. Soil samples were only collected at two locations and were analyzed for BTEX. Four soil and groundwater samples were also collected for microbiological analysis.

Generally, background levels of dissolved oxygen were approximately 2.0 to 3.5 mg/L. Levels downgradient and within the plume were 0.8 to 1.7 mg/L. Measured values of pH were essentially neutral indicating a favourable environment for microbiological growth. Redox potentials ranged from –12mV to –39 mV indicating a slightly reducing environment. Terminal electron acceptor analysis indicated aerobic conditions upgradient of the spill areas, a narrow zone of nitrate utilization beyond the area where oxygen was depleted, a much larger zone of sulphate utilization, and finally, a zone of methane generation. Figure 4-6 shows the different zones of terminal electron acceptors.

A most probable analysis method was used to enumerate microbiological populations at the site. Counts were made of aerobic microorganisms, fuel hydrocarbon utilizing

Figure 4-6. Monitoring Well Locations and Terminal Electron Acceptor Zones at a Petroleum Tank Farm and Refueling Facility in Northeastern Alberta (after Biggar, 1998)


Nitrate Utilization
Carbon Dioxide Utilization
(methanogenesis)
N
GENERAL TOPOGRAPHY SLOPE
405
403
415
UA1-4
UA5-8
420
420-D
416
416-D
419
OIL DRUM STORAGE
BUILDING 385
Sulfur Utilization
(nitrate depleted)
LEGEND
-D
DEEP MONITORING WELL BY THURBER ENVIRONMENTAL
1
TEST HOLES BY THURBER ENVIRONMENTAL (1 THROUGH 30 SERIES)
LOCATION OF FORMER TANK
UNIVERSITY OF ALBERTA MONITORING NESTS
2
MONITORING WELL BY THURBER ENVIRONMENTAL (1 THROUGH 30 SERIES, 416-D & 420-D)
404
MONITORING WELL BY AGRA EARTH & ENVIRONMENT (400 SERIES)
LOCATION OF EXISTING TANK
UNIVERSITY OF ALBERTA TEST HOLES
ORIGINAL BASE PLANS — DWGS A15DP-20, A15EP-20, A15EU-20, A15FP-20, A15FU-20, A15KP-20, A15KU-20
SCALE = 1:2500

microorganisms, and nitrate, sulphate and ferric iron reducing components of the microbiological population. Numbers of iron-reducing microorganisms were low indicating that they would not be important to the intrinsic remediation process. It should be noted that in Figure 4-6 there is no iron-reducing electron acceptor zone. To evaluate aerobic rates of degradation in the lab, fuel samples were spiked with small amounts of radio labeled benzene or toluene. During degradation, the amount of radio labeled $^{14}CO_2$ was measured which indicated the amount of benzene or toluene that had been completely mineralized to CO_2. From this number, the amount of benzene or toluene that had been degraded at a number of time intervals was calculated and from those calculations, the rate of degradation was determined. First order rates of 0.005 day^{-1} and 0.004 day^{-1} were estimated for benzene and toluene, respectively. Tests were also conducted to determine reduction of nitrate, ferric iron, and manganese and generation of methane, CO_2, and ferrous iron.

Modeling of the groundwater flow and fate and behavior of benzene and toluene was conducted using Bioscreen, Modflow, and MT3D. Model results were compared with field measurements of water table and contaminant concentration. These fate and transport models were considered conservative in that they tended to over predict the concentrations of dissolved phase contaminants and the length of the contaminant plume.

The results of the 1997 investigation indicated (Biggar, 1998):

- Elevated concentrations of BTEX in groundwater are not observed in significant quantities more than 100 metres downgradient
- Microbiological activity was ongoing and progressive depletion of terminal electron acceptors was as expected
- A viable population of aerobic and facultative heterotrophic bacteria and nitrate reducing bacteria exists at the site and within the contaminant plume
- Groundwater velocity at the site was approximately 10 m/yr. At this slow velocity, slower rates of microbiological growth due to colder groundwater temperatures

appear to be acceptable to degrade BTEX contamination before it migrates far from the source

- Intrinsic bioremediation appears to be a viable remediation alternative. However, monitoring should continue on a regular basis to ensure that natural attenuation processes are continuing as predicted

4.2 CASE STUDY REVIEW AND DISCUSSION

Protocols and policies in the United States (e.g. USEPA, 1998, 1999, and Wiedermeier et al., 1995) have the clearest guidelines and requirements for information submitted to support an application for use of natural attenuation at a site. Other agencies such as those in Canada and Europe have a less formal approach or base their reviews on the requirements of protocols from the United States. Ontario's "reasonable use" policy (MOEE, 1994a) could be used as a general guide when assessing sites where natural attenuation may be applied. However, this MOEE policy is based solely on the use of groundwater adjacent to a contaminated site. It provides no specific guidance for determining data requirements or the evaluation process for any site characterization, geochemical or biological data obtained during a site investigation. This means that a regulator could accept natural attenuation for a site based only on an evaluation of groundwater use. There would be no consistent advice as to what information to supply or how that information would be evaluated. Therefore, protocols from the USEPA will be used in evaluation of the three case studies in Alberta.

Essentially, three lines of evidence must be evaluated and confirmed by a proponent to ensure adequate information is presented for natural attenuation to be considered at a site. Therefore, the case studies will also be reviewed against those lines of evidence which are:

- Historical data demonstrating a decreasing trend in contaminant mass or concentration other than due to dispersion and dilution

- Hydrogeologic and geochemical data to indicate that natural attenuation processes are viable
- Biological data to confirm that natural attenuation processes are viable

4.2.1 DECREASING TRENDS IN CONTAMINANT MASS OR CONCENTRATION

Site A

Site A has been monitored since 1984 providing 15 years of data on the fate and behavior of the contaminants. Since 1996, quarterly data have been collected specifically to provide an evaluation of potential natural attenuation processes at this site. Analytical information for both soil and groundwater indicate decreasing contaminant concentrations with distance from the source as well as decreasing concentrations with time at various monitoring locations downgradient from the source. Previously collected data have also been re-evaluated to examine trends in contaminant concentration and movement. This amount of information and the length of time over which data have been collected would be sufficient to meet the requirements of the protocols. In addition, information on migration of the contaminants indicates that losses due to plume spread are not significant.

Site B

Nine wells in the vicinity of the hydrocarbon release have been monitored at varying degrees of regularity since 1993. For some wells, the amount of data is sufficient to make conclusions regarding possible trends in analytical parameters. For other wells, sufficient continuous data are unavailable which makes evaluation of trends difficult. Review of these data provides no evidence of loss of contaminant mass or concentration over time. Concentrations of benzene in well 440-8B-SL and other wells fluctuate with time without any indication of a continuously declining trend or steady state. These data could indicate that source control measures are needed and that extent of the dissolved plume must be further defined.

Site C

Site C has been investigated four times since 1993, though only the two most recent investigations were designed to collect data for evaluation of natural attenuation. In this regard, site C does not strictly have enough information to define a trend in contaminant loss due to natural attenuation processes. Contaminant concentrations in groundwater were shown to decrease significantly with distance from the source and concentrations also decreased from 1993 to 1997. This provides an indication that the plume is not spreading and that concentration losses are not due to the migration of the plume. Some preliminary trend information could be determined from the hydrocarbon data based on the four sampling events, however, further monitoring is required to confirm these preliminary results. In the absence of additional contaminant concentration data, geochemical and microbiological data as well as fate and transport modeling information could be examined to determine whether natural attenuation processes are effective in reducing contaminant levels in groundwater. As the monitoring of the plume is ongoing as part of the MNA procedure, evaluation of data downgradient along the plume centerline can also continue. This would fulfil the requirement for historical data.

4.2.2 INDICATIVE GEOCHEMICAL DATA

Site A

Geochemical data have been collected from 26 locations quarterly since 1996. Groundwater samples are analyzed for contaminants of concern, terminal electron acceptors, degradation byproducts, EC, Eh^{o}, pH, and temperature. Terminal electron acceptor analysis indicates distinct aerobic and anaerobic zones downgradient of the source area. These zones are relatively stable with minor variations occurring seasonally.

Geochemical data for Site A provide a clear indication that natural attenuation processes are likely ongoing at this site. Electron acceptor zones are clearly defined and supported by other information such as oxygen consumption and carbon dioxide production studies. Based on the data requirements of Texas (TNRCC, 1997) and Michigan (MDEQ, 1998b), the amount of geochemical data collected from this site would be sufficient to confirm viable natural attenuation processes. Any further monitoring could concentrate on evaluation of contaminant reduction rather than on gathering evidence to satisfy the second line of evidence. Modeling of the site has not been conducted. This should be done in order to provide an additional evaluation of the indicated degradation processes.

Site B

Review of the TEA data does not strongly support the main conclusion of the proponent which is that natural attenuation is a viable process at this site. Changes in TEA concentration in most of the wells generally do not appear to correspond with changes in contaminant concentration, nor can distinct TEA zones be delineated with available data. For well 440-8B-SL, higher sulphate levels appear to correspond with low benzene levels while lower sulphate levels correspond with higher benzene levels (see Figure 4-4). This is not an indication of sulphate reduction of benzene below concentrations of 20 mg/L. If sulphate reduction were occurring, sulphate levels should decrease with decreasing benzene levels. Monitoring for hydrogen sulphide would determine whether sulphate reduction was taking place. Reduction in sulphate levels at higher benzene concentrations could indicate that these concentrations are toxic to sulphate-reducing bacteria. Manganese and iron (II) concentrations appear to follow a similar pattern (see Figure 4-5). Nitrate levels were reduced to near zero in 1995 and have remained low regardless of benzene concentration. This could be an indication that denitrification is a main biodegradation pathway. However, background nitrate concentrations are not available for comparison.

Modeling of the site to examine contaminant fate and transport as well as changes in TEA concentrations has not been conducted since the original risk assessment. This information together with more consistent monitoring would provide greater insight into biodegradation processes at other monitoring well locations as suggested by data from well 440-8B-SL.

Site C

Groundwater samples were collected at site C from 15 drive point sampler locations in addition to the 8 monitoring wells installed in 1997. Samples were analyzed for contaminants of concern, terminal electron acceptors, biodegradation products, pH, EC, Eh^{o} and temperature. These parameters are in accordance with USEPA (USEPA,1999), DOD (Wiedermeier et al., 1995), and ASTM (ASTM, 1998) protocols.

Limited geochemical data for Site C provide a preliminary indication that natural attenuation processes, primarily biodegradation, are viable at this site. Oxygen levels are depleted in the contaminant plume as compared to background levels (2.0 to 3.5 mg/L versus 0.8 to 1.1 mg/L respectively). Redox values within the plume indicate a slightly reducing environment and pH levels indicate conditions suitable for microbiological growth. Terminal electron acceptor analysis indicates clearly defined anaerobic electron acceptors zones beyond the zone of oxygen depletion. Comparison of modeling results with field data indicates that predicted rates of contaminant loss and potential plume migration distances are consistent with conditions in the field. While preliminary in nature, the geochemical and hydrogeological data strongly suggest that natural attenuation processes are viable at this site.

The geochemical evidence for Site C is based on one sampling event. Neither the USEPA nor DOD protocols specify an appropriate number of sampling events necessary for proper determination of geochemical parameters. The Texas protocol (TNRCC, 1997) requires a minimum of four sampling events and Michigan (MDEQ, 1998b) requires a minimum of eight consecutive quarters of monitoring to properly characterize geochemical parameters. Meeting these requirements would provide some information on seasonal variability in both plume and process behavior. Because a common theme in the application of natural attenuation is the protection of potential receptors, a single sampling event would not provide adequate information to assess either the processes involved or their ability to protect adjacent receptors. Therefore, additional, consecutive monitoring events are warranted.

4.2.3 BIOLOGICAL DATA

Site A

Microcosm studies have not been conducted for Site A. Therefore, until this information is provided, natural attenuation would not be considered under USEPA or DOD protocols. ASTM protocols do not require microcosm studies to be completed in order for natural attenuation to be considered at a site. Oxygen consumption and carbon dioxide production data lend support to arguments regarding the presence of microorganisms capable of degrading contaminants of concern. It could also be argued that geochemical data provide an indication of the microbiological population. However, actual enumeration studies provide confirmation of the types and numbers of microorganisms as well as some information for predicting the duration of monitoring required to achieve remediation requirements.

Site B

Most probable number data for samples collected from four of the nine monitoring well sites indicate that microbiological populations are increasing with time. Types and distributions of the populations have not been examined. These data would provide an indication of what microorganisms are responsible for contaminant degradation and what substrates the microorganisms are utilizing. In addition, field degradation rate studies would be useful for determining a potential timeframe for remediation of the contaminants and to determine if natural attenuation is indeed protective of potential receptors. Further investigation would be required to provide enough information to satisfy requirements for this line of evidence.

Site C

Soil and groundwater samples were collected for microbiological analysis upgradient of the contamination, within the contaminant plume, and downgradient of the plume. Aerobic plate counts and aerobic and anaerobic most probable number analysis for microorganisms were conducted. Results indicate that viable populations of contaminant degrading and nitrate reducing microorganisms exist both upgradient and downgradient of very near the source area. Populations were diminished within the plume. Previous geochemical analysis indicated that denitrification was the dominant anaerobic process involved in degradation of the contaminants. This was confirmed by microbiological mineralization studies conducted on the contaminants. A zone of decreasing sulphate concentrations in groundwater was also identified, but sulphate-reducing bacteria were not identified by the microbiological analyses.

Generally, the biological information indicates that viable populations of contaminant degraders are present at this site. This information satisfies the third line of evidence. However, discrepancies between geochemical and microbiological data would need to be addressed before establishing final parameters for a long term monitoring program for this site.

4.2.4 SUMMARY

Each of the case study sites has some measure of potential natural attenuation processes occurring. The site with the least potential is Site B, mainly because of lack of available data. However, even at this site, some potential for natural attenuation is demonstrated by correlation between decrease in contaminant and TEA levels at one of the monitoring locations. These case studies demonstrate that natural attenuation processes, and in particular biodegradation processes, can occur in native Alberta soils and under Alberta climatic conditions. Site C demonstrates that biodegradation processes are viable even at lower than “favourable” temperatures. This means that natural attenuation can be considered a potential remediation option in Alberta provided that the appropriate parameters are thoroughly examined during the site, contaminant, geochemical, and microbiological characterization stages.

Using lines of evidence to evaluate data submitted in support of natural attenuation is an excellent method for determining natural attenuation potential at a site. All three lines of evidence (historical, geochemical, and biological data) must be reviewed so that the full potential for natural attenuation at a site is evaluated. If only the first two lines of evidence are examined, as required by the ASTM protocol (ASTM, 1998), natural attenuation may be dismissed as a remediation option. For example, at site B, historical and geochemical data alone do not support the potential for natural attenuation. However, when biological data are examined, some potential for natural attenuation is identified.

The line of evidence review has indicated potential for natural attenuation at all three case study sites in Alberta. However, for natural attenuation to be approved as a remediation option in Alberta based on USEPA and DOD guidelines and protocols, the following information would be required:

- **Site A** – Microcosm studies to provide confirmation of biodegradation processes and rates of degradation
- **Site B** – Evaluation of source control; additional investigation to provide reliable trends in contaminant concentrations, confirmation of loss of contaminants, confirmation of natural attenuation (particularly biodegradation) processes, and confirmation of microbiological activity
- **Site C** - Further monitoring to confirm trends in contaminant loss

5.0 RECOMMENDATIONS FOR IMPLEMENTATION OF MONITORED NATURAL ATTENUATION IN ALBERTA

Research into natural attenuation of fuel hydrocarbons, its proven ability to effectively remediate sites, and restrictions and provisos placed on its use have been adequately evaluated by other agencies in United States. In instances where U.S. states have developed their own policy and guidance, information required by those policies or guidances does not vary significantly from that required by the USEPA. State guidances do differ in the remediation objectives that must be met. Alberta's remediation objectives may also vary from the U.S. state objectives due to factors such as "likelihood of impact" or concerns about aquifer vulnerability. However, U.S. remediation objectives should be reviewed and compared to Alberta conditions in a manner similar to natural attenuation before deciding on final remediation objectives for Alberta. Regardless, natural attenuation must be proven effective at protecting sensitive receptors and the environment.

The United Kingdom is at the same stage in policy and protocol development as Alberta. The Environment Agency in the United Kingdom will be adapting the USEPA protocols with changes to account for differing geology, hydrogeology, and climate. Development of the United Kingdom protocol should be closely followed to assist Alberta in understanding how changes can be made to USEPA, DOD, or U.S. state documents, should they also be adopted for Alberta.

Monitored natural attenuation (MNA) should not be viewed as a presumptive remedy or as a "do-nothing" type remedy. MNA is one of several remedial options available and must be thoroughly evaluated prior to acceptance or implementation. The success of natural attenuation at sites in United States should not be taken to mean that natural attenuation will automatically be successful in Alberta. A candidate site for MNA needs to be thoroughly investigated, and monitoring and verification are keys to allowing natural attenuation to be implemented at a site. It should not be seen as an option whereby proponents are able to avoid their responsibilities and obligations for site remediation. Regulators in the U.S. states require specific groundwater and soil remediation objectives to be met (e.g. MDEQ, 1996, UDEQ, 1999, NHDES, 1998). This should be the same case in Alberta.

Proponents are keen to implement MNA at some of their contaminated sites in Alberta (Nason, 1999). It is recommended that any policy regarding MNA and related guidelines or protocols be presented for industry review and comment particularly from industries with experience in implementation of MNA in the United States. Alberta could gain insight on the workability of USEPA or state legislation that may be under consideration for adoption.

The following recommendations are seen as key to effective policy development for the use of MNA in Alberta.

Recommendation 1 – Adopt Existing Hydrocarbon Directives

It is recommended that the USEPA directives for MNA at underground storage tank sites (USEPA, 1999) be adopted and modified as necessary rather than developing an entirely new directive as policy for Alberta. Requirements for site characterization, sites where MNA may be appropriate, contaminants of concern, reasonable timeframes, and performance monitoring and evaluation should be expanded to address specific conditions related to Alberta's geology, climate and resource use. Pertinent aspects from other publications such as the ASTM Guide (ASTM, 1998) or the DOD technical protocols (USEPA, 1998,1999) should also be included in the Alberta policy. Care must be given to ensure that Alberta policy adequately reflects requirements of existing legislation in Alberta related to site remediation and land use. Co-ordination is required not only for legislation residing with Alberta Environment but also the Alberta Energy and Utilities Board, Alberta Municipal Affairs, Alberta Labour, and municipalities.

Recommendation 2 - Lines of Evidence

All agency documents reviewed require the proponent of MNA to provide information that satisfies lines of evidence. Lines of evidence are used to evaluate efficacy of MNA at a site. **AENV should use the three lines of evidence required by the USEPA Directive (USEPA, 1999) and Protocol (USEPA, 1998) rather than the ASTM Guide (ASTM, 1998) which only recommends two lines of evidence.** In the ASTM Guide, microbiological information is seen as secondary or optional information. However, as MNA relies heavily on biodegradation for the removal of contamination, AENV must require that this information be provided by the proponent. In situations where historical data is not available but geochemical data, microbiological data, and modeling are supportive of MNA, MNA could be regarded as viable. Groundwater monitoring data collected within the plume and at sentry wells during further evaluation of MNA could be used to fulfil the requirement of historical data without holding up the process while waiting for more data.

Recommendation 3 – Source Removal

Where feasible, it is recommended that AENV require source removal due to potential human health and environmental concerns, and potential toxicity to microorganisms that may play a role in reducing contaminant concentration. Non-implementation of source control may eliminate consideration of MNA as an option as it may result in an increased timeframe for remediation objectives to be met and ongoing potential problems, such as volatization of hydrocarbons and vapour migration into buildings, caused by the source remaining in place. It must be established that the plume associated with contamination is stable in the short term or, preferably, shrinking. An increasing or long-term stable plume is seen to be evidence of inadequate source control and a potentially long remediation time. For historical contamination events, MNA could be considered as a means of dealing both with the source and plume. It must be noted that source removal is not always easy or effective. Free product can be trapped in pore spaces or fractures within the vadose zone or aquifer matrix and act as a continuous, long-term source of dissolved phase contaminants.

It may not be necessary to remove free product in every situation. Studies in Texas by the Bureau of Economic Geology (Mace et al., 1997) found that use of active groundwater remediation at leaking petroleum storage tank sites did not result in a lower median plume length than at sites where source control did not occur. Therefore, removal of obvious sources such as a leaking storage tank or repair of a leaking pond liner must be undertaken. Effective removal of free product is recommended but its necessity could be evaluated on a case by case basis.

Recommendation 4 - Post-Implementation Monitoring

It is recommended that natural attenuation only be considered for a site with an accompanying monitoring and evaluation program. Due to uncertainties involved in defining efficacy of natural attenuation, monitoring and evaluation are required to prove predictions made during a feasibility study conducted for MNA. Proponents of natural attenuation must identify processes active at their site and design a monitoring program to account for any intermediates of biodegradation.

Recommendation 5 - Approval Process

It is recommended that implementation of MNA be governed by an approval process due to the amount of time required both on the part of the proponent gathering information required to support use of MNA and the regulator reviewing the information. An approval allows the monitoring and evaluation process to be clearly spelled out to a proponent (and regulator), as well as contingency measures and triggers for implementation of those measures. An approval process ensures that remediation objectives are met especially in situations where site-specific remediation objectives are used. Proponents would be required to demonstrate that objectives have been met before closure is granted. The approval also gives regulators the ability to enforce remediation should problems occur during implementation of a remediation program or should the regulator need to institute contingency measures when it is demonstrated that natural attenuation is not working at a site. Any application for MNA as part of the approval process must provide the following:

- Comprehensive site characterization
- Comprehensive contaminant characterization
- Adequate feasibility evaluation
- Comprehensive development of a performance monitoring and evaluation program
- Comprehensive development of contingency measures and trigger criteria for implementation
- An acceptable remediation plan for source removal or control

Recommendation 6 - Offsite Migration

Existing AENV guidances do not allow for impairment of property use by migration of contaminants onto adjacent properties without landowner consent (AENV, 1999b). **In case of offsite migration, affected party consultation and their acceptance of property impairment must be documented.** If the landowner does not give consent, remediation of offsite contamination must meet applicable regulatory criteria.

Recommendation 7 – Include Landfills

It is recommended that the policy on MNA be expanded to include reviews of landfill developments. The current Alberta Code of Practice for Landfills (AENV, 1998) subtly indicates that natural attenuation could be considered as an alternate design to a liner/leachate collection system for the landfill. However, no clear guidelines are presented for evaluating the alternate design. Many of the site characterization and evaluation items in the protocols for hydrocarbons or chlorinated solvents could also be adapted for evaluation of the attenuation of landfill leachate.

When developing the policy on MNA, there are other items that need to be addressed. The following additional recommendations should be also be considered and included in the final policy.

Recommendation 8 – Responsible Use

Onus must be placed on industry and the Alberta government to avoid using or accepting MNA as a presumptive remedy for contaminated sites. Care must be taken not to overwhelm the regulator, Alberta Environment (AENV), with a flood of applications for its use at many potentially unsuitable sites. This happened with risk assessments in the early 1990s and as a result, some of those early risk assessments lost some respect in both the public's and regulator's eyes as a viable scientific process. Since that time, risk assessment proponents have concentrated on the science behind the assessment resulting in much greater acceptance of the findings.

Recommendation 9 – Test Cases

The first few sites where an application is made to use natural attenuation should be used as test cases for a thorough examination of the feasibility and efficacy of MNA in Alberta. While case studies examined in this document suggest that MNA may be feasible, the examinations performed did not fulfil the requirements of some of the most current legislation/guidance in the United States.

Recommendation 10 – Supporting Scientific Information

AENV must be clear regarding the scientific requirements for support of MNA so that proponents understand there are strict informational requirements for its use. Conard (1999) indicated that although natural attenuation was widely encouraged when it was first accepted as a potential remediation option in Texas, its use is now highly restricted. This was due to numerous poor site characterizations and lack of proper or adequate information provided by the proponent or their consultant. Texas reimburses proponents for expenses related to petroleum storage tank remediation and therefore lack of proper information was seen as an abuse of the reimbursement fund.

Recommendation 11 – Use Existing Protocols

Protocols published by the USEPA and DOD for gathering site information (USEPA, 1998, 1999 and Wiedermeier et al., 1995) for the above application requirements should be followed in Alberta. These protocols are comprehensive guides which have been adequately proven at sites where MNA has been accepted and implemented. As discussed above, there are some problems with the scoring system for sites involving chlorinated solvents. **Therefore, it is recommended that parameters specified in the USEPA's scoring system (USEPA, 1998) be made into a checklist for Alberta regulators to ensure that proponents will properly evaluate sites where chlorinated solvents are released.** This checklist would also ensure a consistent review on the part of regulators in Alberta's six different regions.

Recommendation 12 – Consistency of Delivery

It is recommended that consistency of an MNA policy delivery be addressed. There must be adequate training of regulators in the six Alberta Environment regions on natural attenuation processes and information required to support a successful application for use of MNA at a site. This will ensure that use of MNA is supported by sufficient site-specific information. Regulators must also be willing to require that proponents follow protocols and informational requirements necessary to support verification and implementation of MNA. There may be site-specific remediation objectives set for each site under consideration, however, types and amounts of information required, process for proving efficacy of MNA, and process for verification of MNA at a site do not change. Regulators must be satisfied that MNA will fully protect potential human and environmental receptors and that site remediation objectives can be met within a reasonable timeframe.

Recommendation 13 – Site Characterization Guidance

Much detail on collection of information for site characterization, model evaluation and microorganism studies is provided in the USEPA (USEPA, 1998, 1999), DOD (Wiedermeier et al., 1995) and ASTM (ASTM, 1998) documents. **These documents should be referenced in Alberta policy as a technical resource for proponents, consultants, and regulatory personnel involved in evaluating applications for MNA at a site.**

Recommendation 14 – Thorough Site Characterization

It is very important for the redox conditions in an aquifer to be accurately delineated particularly when dealing with chlorinated ethenes as a contaminant of concern. This is because the reducing process affects the efficiency of reductive dechlorination. Therefore, **it is essential that thorough site characterization data form part of any proposal for MNA.** Because of the amount of detail required to adequately characterize a site under consideration for natural attenuation, proponents must be made fully aware of specific information required by the regulatory body. Checklists from Minnesota (MPCA, 1997) or Utah (UDEQ, 1999) should be adopted by AENV and used to ensure that required information is provided.

Recommendation 15 - Timeframe for Completion

It is recommended that a reasonable time limit be placed on completion of MNA processes and achievement of remediation requirements. This may discourage proponents who are not concerned about establishing a long-term monitoring program or situations where sites will be monitored ad infinitum with no real desire to bring them to closure. The problem comes from deciding what constitutes a reasonable time frame. Regulators in United States base the time frame on a comparison with other viable remediation technologies except for New Hampshire (NHDES, 1998) which places a time limit of ten years on the use of MNA. In Alberta, time frames for natural attenuation to achieve remediation objectives are likely to be longer due to the nature of clay and glacial till soils often found at sites. Therefore, **the time frame should be based on receptor proximity and sensitivity to contaminant exposure combined with travel time approximations from fate and transport modeling.** In situations where the regulator does not consider the proposed timeframe to be reasonable, a proponent should review the efficacy of enhancing the attenuation processes as a means of reducing the timeframe required for remediation.

Recommendation 16 – No Receptor Remediation Timeframes

For situations **where no receptors are likely to exist, consideration should be given for increasing the timeframe for closure.** For these longer-term sites, it is recommended that a financial bond should be required to ensure that proponents continue with proper monitoring and data evaluation, and that sufficient funds are available should a contingency plan be required.

Recommendation 17 – Fractured Soils

The potential for organic contaminants or free phase liquids to diffuse into clay or bedrock matrix materials suggests that **natural attenuation may not be appropriate for**

sites where short-term solutions are required for remediation. This is because of the time required for contaminants to migrate back out of the matrix and into the fractures. Natural attenuation at sites involving contamination migration into tight clays or fractured bedrock could be favourable where long-term remediation is not a concern. In this instance, it is recommended that monitoring continue well after the documented disappearance of contamination due to reverse diffusion from the matrix to the groundwater.

Recommendation 18 - Public Consultation

As with any new environment policy or regulation, **it is recommended that natural attenuation policy be presented to the public and other stakeholders for review and comment.** Public input must be sought at the beginning rather than at the end of the policy and regulation development stage. It is important to stress that there is science behind the remediation method so that the public's suspicion of another "do-nothing" approach to site contamination can be proactively addressed. Information bulletins such as those prepared by the USEPA (USEPA, 1996b) can be presented to stress what MNA is prior to discussion of policy.

Recommendation 19 – Affected Party Buy-In

The public must be made aware that directly affected parties will have input into use of MNA in the case of offsite contamination or lease sites. **In situations where MNA is proposed for a lease site, the proponent must have buy-in from the property owner for AENV to accept its use.**

Recommendation 20 – Registration Process

Issuing approvals to the numerous oil and gas lease sites in Alberta would be an onerous task without additional manpower. However, until studies examining efficacy of MNA under Alberta conditions are complete (see below), approvals may be the only way to ensure that implementation of MNA is handled correctly. **Once studies are complete and regulators are comfortable evaluating MNA as a remediation option, AENV should consider registration of smaller sites such as oil and gas leases.** Checklists could be developed to ensure that adequate information is supplied to the regulator by a proponent. However, because these sites are leased, proponents would still require documented consent of the property owner before implementing MNA.

Recommendation 21 – Public Participation in Approval Process

As with any approval process, approval of MNA use at a site by AENV should undergo public consultation. Directly affected parties must be allowed to have input into the review process and be given the right to appeal a decision. This can be determined on a case-by-case basis. The proponent must provide documentation that it has met, and explained MNA to the stakeholders. In situations where contamination occurs on Crown Land, AENV should be considered to act on behalf of the affected party.

Recommendation 22 - Post-Implementation Monitoring

A comprehensive post-implementation monitoring program must form part of any approval for use of natural attenuation at a site. The concept of performance and compliance monitoring as developed by the USEPA in its chlorinated solvents protocol (USEPA, 1998) should be considered for Alberta sites. The monitoring program must be coupled with a clearly defined contingency plan that will be implemented at a site if warranted. Trigger criteria such as those provided in USEPA (1999) should be clearly spelled out in the monitoring program.

Recommendation 23 - Other MNA Components

Should a policy on natural attenuation include metals, **requirements for evaluating natural attenuation of metals should be incorporated into a protocol document.** For example, Palmer and Puls (1994), provided a discussion on natural attenuation of hexavalent chromium in groundwater and soils. They suggested that for natural attenuation to be considered at a site contaminated by hexavalent chromium, five items must be demonstrated:

- There are natural reductants present within an aquifer
- Amount of chromium (VI) does not exceed the capacity of an aquifer to reduce them
- Rate of chromium (VI) reduction is greater than rate of transport of aqueous chromium (VI) from the site
- Chromium (III) remains immobile
- There is no net oxidation of chromium (III) to chromium (VI)

Although soil has a significant capacity to attenuate toxic heavy metals using a variety of physical, chemical, and biological processes, those processes do not appear to create proven permanent attenuation. Therefore, sites where natural attenuation is being considered as a remediation option for heavy metals must have adequate monitoring programs and adequate controls over site use that will prevent the remobilization of the metals and provide early warning of changes to subsurface conditions.

Alberta's Code of Practice for Landfills (AENV, 1998) indicates that an alternate design to an engineered design can be proposed. The alternate design must ensure that specific parameter concentration objectives are met at compliance points around a landfill. Details for the process of proving that a site can achieve these objectives have not yet been developed. However, some aspects of the existing natural attenuation protocols such as microbiological studies, terminal electron acceptor studies and fate and transport modeling could be used to evaluate the potential for leachate attenuation at a proposed landfill site.

Institutional controls such as caveats on land titles could be considered in situations where contamination extends offsite or for sites where timeframes are expected to be extended. This would ensure that the proponent continues their role in site remediation and that future developers are aware of the active remediation when designing new developments on a site where natural attenuation has been implemented. As discussed above, site development can affect the efficacy of natural attenuation. Therefore, regulators need a mechanism to allow input into site redevelopment so that redevelopment does not create problems at natural attenuation sites. In situations where natural attenuation will be affected, the developer may be required to implement another remediation technology.

5.1 FURTHER RESEARCH TO EVALUATE MNA EFFICACY IN ALBERTA

Follow-up discussions with regulatory agencies is recommended particularly if one or more of the existing policies and protocols are used to develop policy and protocols for Alberta. Although some effort was made to discuss policy development and positive and negative aspects of existing legislation, discussions were not as extensive as desired. It is also recommended that some contact be made with consulting companies working in the United States to obtain their experiences with existing Federal and State legislation.

Although protocols and guidances exist for use of natural attenuation at sites contaminated by chlorinated solvents, additional research is required to define the effectiveness of processes on remediation of these solvents in the field. Further research is also required to examine the effectiveness of natural attenuation process in Alberta conditions of soil and groundwater temperature, geology, and climate.

Existing USEPA, DOD and ASTM protocols seem to deal with an ideal site where soils are sandy or silty. These types of sites are easier to characterize in terms of hydrogeology and geochemistry (due to their ease of monitoring), and they are easier to model (due to their homogeneity). The protocols do not discuss differences in dealing with heavy clay or glacial till soils or sites with shallow, fractured bedrock. These sites have inherent problems of heterogeneity, requiring more comprehensive site characterization and monitoring. Fractures in clays and changes in hydraulic conductivity within glacial tills require closer spacing of monitoring wells during site characterization and verification of modeling results. Groundwater samples can be more difficult to collect in glacial tills due to slow well recoveries. These sites are generally more difficult to accurately model. Because clay and clay till soils are prevalent across Alberta, any protocol adopted or developed would need to address special requirements of these types of soils for proving the potential of natural attenuation. Specifically, the following items characteristic of Alberta conditions and their effect on the efficacy of natural attenuation, and sampling or site characterization requirements need further research and evaluation:

- Shallow fractured bedrock
- Tight clay or clay till soils
- Salt plumes associated with contaminants at site such as oil and gas lease sites or pipeline spills
- Low organic carbon content in soils
- DNAPL diffusion into and out of clay soils
- Low temperatures for biodegradation

Information gained by studies on these items should be incorporated into any protocol adopted or developed for Alberta.

Many studies on natural attenuation deal with contaminants associated with downstream oil and gas facilities. In Alberta, natural attenuation may be applied to a large number of upstream facilities where process chemicals may influence the effectiveness of natural attenuation processes. Additional research is needed to evaluate natural attenuation at these types of sites.

Even if AENV accepts MNA as a remediation option, further AENV needs to develop criteria for evaluating use of MNA in terms of site performance and specific remediation objectives. Items to consider include:

- No off lease or offsite migration of contaminants at concentrations greater than groundwater quality objectives. Some regulators allow offsite migration provided that protection of potential receptors is ensured by MNA. In keeping with AENV's current position on risk assessment, acceptance of offsite migration exceeding acceptable limits would be contingent on verified acceptance by a property owner(s)
- Acceptable hydraulic conductivity and groundwater flow velocity values. Further study should determine if there are values for these factors that would preclude the use of natural attenuation. As discussed above, these factors can affect the effectiveness of MNA processes. If the basic premise is that MNA must be protective of human health and the environment, then acceptance of MNA must be based on its ability to perform accordingly. In that case, factors such as site geology and hydrogeology are accounted for in steps leading up to regulatory approval of MNA at a site. Proponents of MNA must understand the need to properly characterize a site and the need to provide clear evidence of the potential success of MNA at a site
- Evaluation of minimal source removal or control actions
- No degradation of aquifer quality. MNA must be fully protective of the water resources in the Province. Immediate threats to potable groundwater or surface water supplies indicate that a more rigorous remediation program may be required. If it can not be clearly demonstrated that MNA is protective, it must not be accepted for use at a site
- Stable or shrinking plumes. Continued migration of a contaminant plume is an indication that MNA may not be appropriate for a site and that other more active approaches to remediation may be required. The extent to which a plume migrates must be assessed in terms of potential impact to receptors

- Reduction in contaminant level. MNA must not be allowed to continue forever. Rather, there must be a demonstrated reduction in contaminant mass or concentration over the duration that MNA is employed at a site. MNA must be able to achieve applicable groundwater or soil performance criteria
- Time limit for success. All of the regulatory agencies require that MNA be successful within a time period comparable to that of other applicable remediation methods. MNA cannot compete with "dig and dump" scenarios or with pump and treat technologies in some situations. However, at sites where alternate technologies have a limited potential for short-term success, MNA may be a viable option. In Alberta, approvals are issued for a maximum ten year period. If a maximum ten year period was also specified for natural attenuation to meet objectives at a site, the MNA process would be covered by one approval
- Performance criteria. Currently, AENV requires a more comprehensive set of soil or groundwater performance criteria. Alberta Tier I and Canadian Water Quality Guidelines criteria provide only a limited set of protective criteria for sites. AENV must work towards developing or adopting a full set of criteria covering all potential priority contaminants in conjunction with enacting legislation regarding MNA. Several states have comprehensive criteria that could be evaluated and adopted by AENV.

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APPENDIX A

QUESTIONNAIRE

1. **Does your state have a policy on natural attenuation?**

2. **If so, is it a guideline, regulation, or code of practice?**

3. **Did your state develop its own policy or did it adopt the USEPA's policy?**

4. **If your state developed its own policy, how was this done?**

5. **What were the positive and negative aspects of developing the policy?**

6. Were the public or other potential stakeholders consulted on the policy? If so how?

7. Has there been any opposition to the policy or its implementation? If so what?

8. How, or for what types of contaminants and sites, has natural attenuation been used? Could I obtain a case study on one site?

9. Who makes the final decisions on the use of natural attenuation?

10. Does a proponent formally apply to the government to use natural attenuation at a site?

11. **If the "application " is accepted, is an approval issued to the company with specific monitoring or reporting requirements?**

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12. **Do adjacent property owners have any input into the decision making process? Can they appeal a decision?**

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13. **Is site monitoring always a requirement when natural attenuation is applied to a site. What reporting requirements are involved?**

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14. **Are there situations where natural attenuation will not be considered regardless of the evidence in favour/support or its potential?**

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15. **If natural attenuation is rejected as an option in the above circumstance, is it because of site location, time frames involved, type of adjacent receptor or contaminant type or level?**

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16. Do you have any contacts in other states to whom I could address similar questions?

I am hoping that you can provide information on the above or put me in contact with the appropriate person in your department. I would also like to obtain copies of any policy, legislation or guidelines dealing with natural attenuation prepared by your state as well as any background information dealing with the development of those documents.